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ELECTROLYTE EFFECTS ON THE AQUATION OF
BROMOPENTAMMINECHROMIUM(III) BROMIDE

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
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OF MASTER OF SCIENCE

DEPARTMENT OF CHEMISTRY

BY

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The undersigned certify that they have read, and
recommend to the Faculty of Graduate Studies for acceptance, a
thesis entitled

ELECTROLYTE EFFECTS ON THE AQUATION OF
BROMOPENTAMMINECHROMIUM(III) BROMIDE

submitted by L. Neering in partial fulfilment of the requirements
for the degree of Master of Science

ABSTRACT

The effect of perchlorate electrolyte concentration on the rate of aquation of bromopentamminechromium(III) bromide was investigated by a polarographic method. The rate of aquation decreased with increasing electrolyte concentration over the range of concentrations studied with the magnitudes of the decrease being similar although not equal for each electrolyte.

The effect of electrolyte concentration on the rate of aquation was interpreted as a general electrolyte effect. The nature of the electrolyte effect appeared to indicate the importance of at least two contributing factors;

- (a) water participates in the rate determining step and the effect of electrolyte concentration on the activity of water has to be considered.
- (b) the effect of electrolyte concentration on the activity coefficient of the bromopentamminechromium(III) cation has to be considered.

The general participation of water in the rate determining step has been previously postulated in terms of a "solvent assisted S_N1 mechanism".

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I INTRODUCTION

General

The recent revival of interest in the study of inorganic reaction mechanisms in solution has, of necessity, been accompanied by a renewed interest in studies of the behaviour of ions and electrolytes in solution, the role of the solvent, and the effect of inert electrolyte concentration (1). The reason is, that in any but the lowest electrolyte concentrations corrections to the kinetic data for activities, association or ion pairing, and solvation become important (2).

Unfortunately, the nature of both ion - ion and ion - solvent interactions is not yet fully understood, and it is therefore seldom possible to correct kinetic data quantitatively for the accompanying electrolyte effects. Activity coefficients for dilute solutions of a single electrolyte can, in many cases, be accurately predicted. At higher concentrations or in solutions containing more than one electrolyte theoretical prediction of the activity coefficients is usually unsatisfactory and often impossible; in such cases it is often possible to determine mean activity coefficients experimentally, although activity coefficients of individual ions cannot as yet be measured (3). In the case of ion - solvent interactions no satisfactory theory has as yet been developed; for water as the solvent, however, the solvent activity can be determined through the measurement of the osmotic coefficient (4).

When the solvent itself is one of the reactants, as is the case in the aquation of coordination compounds, the dependence of the water activity on the concentration and species of electrolyte present becomes

of special significance. The activity of water is commonly assumed to be unity and water therefore cancels out of all the rate expressions. At any appreciable electrolyte concentration, however, the activity of water will be less than unity, so that, if water participates in the rate determining step of a reaction, the observed rate constant, like the activity of water, will be dependent on the concentration and species of electrolyte. The effect of electrolyte on the activity of water is potentially useful in elucidating the role of water in aquation reactions.

In studying the pH dependence of aquation of the bromopentamminechromium(III) cation it had been observed that below pH=1 the reaction rate decreased with increasing hydrogen ion concentration (5). In order to reach such low pH values it had been necessary to use increased amounts of electrolyte as the pH decreased. The decrease in the rate constant with decreasing pH could therefore be due to either the specific participation of the proton in the rate determining step at high acid concentrations or a general electrolyte effect on the activities of the reactants and possibly also on the mechanism, because of the change in dielectric constant.

The purpose of the work reported in this thesis was to investigate the effect of high acid concentrations on the aquation of bromopentamminechromium(III) cation and identify the results in terms of an electrolyte effect or the possible occurrence of an alternate mechanism.

Aquation Reactions

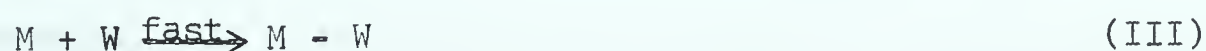
The most common reactions of coordination complexes are nucleophilic substitution reactions, in which one ligand, the nucleophilic reagent, replaces another. The nature of the substituting ligand further categorizes these reactions into solvolytic reactions, where the solvent is the entering ligand, and exchange reactions, where a ligand other than the solvent is the entering species.

Aquation is the solvolytic nucleophilic substitution reaction in which a ligand is replaced by a water molecule, as shown in equation (I).



The interest in the mechanism of the aquation reaction is the result of the belief that, for a ligand exchange reaction in aqueous solution, the reaction goes through the aquated complex, the only possible exception occurring when the hydroxide ion is the attacking ligand (6). The mechanism of the aquation reaction is therefore important in understanding the substitution reactions of coordination complexes.

Nucleophilic substitution reactions, such as the aquation of a complex ion, can proceed by at least two limiting pathways, which are referred to by Hughes and Ingold as S_N1 and S_N2 (7). The S_N1 mechanism has a unimolecular dissociation as the rate determining step, followed by a fast recombination, as shown in equations (II) and (III).



Throughout this treatment the following symbols will be used:

$M - A$, a complex ion with replaceable ligand A. (no charges will be shown).

$M - W$, the corresponding aquo complex.

In an S_N1 mechanism the intermediate, M, has a reduced coordination number.

The S_N2 mechanism has a bimolecular displacement as the rate determining step, as shown in equation (IV).



The intermediate in an S_N2 mechanism has an increased coordination number.

Essentially, the S_N1 mechanism involves bond rupture as the rate determining step and the incoming ligand does not participate in this step. The S_N2 mechanism involves bond formation as the rate determining step and the incoming ligand does participate in this step. It should then be possible to distinguish between these two mechanisms from the fact that, for an S_N1 mechanism the rate of reaction should be independent of the concentration and nature of the incoming ligand, while for an S_N2 mechanism the opposite should be true. When the solvent is the entering ligand, however, the change in its concentration resulting from the progress of the reaction is negligibly small, so that for the aquation reaction the order of the reaction with respect to the ligand concentration cannot be used to determine the mechanism involved.

Alternately, the detection of a reaction intermediate of either a reduced or increased coordination number, corresponding respectively to an S_N1 or an S_N2 mechanism, would be proof of the mechanism involved. Such an intermediate could be very reactive, however, and escape detection because of its short average life time, so that the lack of proof of the existence of such intermediates does not rule out the existence of their corresponding mechanistic pathways.

Despite the considerable effort made in the past decade to assign a mechanism to the aquation reaction, the exact path followed by this reaction is still open to question. This is probably due to the fact that characteristics from both the S_N1 and the S_N2 limiting pathways contribute to the

mechanism, the proportion of the magnitude of their contributions depending on the individual situation. In an effort to understand the mechanism of aquation more indirect methods of approach have been employed (8). Studies of the effect on the reaction rate of the reactant complex composition as well as the environmental composition have been helpful in elucidating the mechanism of the aquation reaction.

On the basis of Ligand Field Theory it has been possible to make semi-theoretical quantitative predictions about reaction pathways and reaction intermediates (9). The Ligand Field Theory is based on the fact that the d orbitals of a central metal atom which are degenerate in the gaseous state, are split in solution as the result of the electrostatic field produced at the metal ion by the solvent environment. Electrons will tend to occupy the low energy orbitals and the gain in energy obtained by preferential filling of these orbitals is called the Crystal Field Stabilization Energy, CFSE. This CFSE can be calculated from the position of the peaks of the visible absorption spectra (10).

Using Ligand Field Theory it is possible to estimate the CFSE for the transition state. This made it possible to estimate the ligand field contribution to the activation energy, which is the gain in CFSE obtained in going from the ground configuration to the transition state. Basolo and Pearson considered different possible configurations for the transition state of a cobalt complex by both S_N1 and S_N2 paths, and calculated the gain in CFSE in forming these different transition states from an octahedral configuration (11). Using the potential energy function and the Born approximation for the hydration energy of the complex ion, Basolo and Pearson calculated the bond energies for the cobalt system as well (12). The activation energies, including the contribution from CFSE, are 121 kcal. for an S_N1 mechanism with a tri-

gonal bi-pyramid structure for the transition state, 103 kcal. for the S_N2 mechanism, and 6 - 94 kcal. for the S_N1 mechanism with a square pyramid transition state structure.

The activation energies for the aquation of cobalt (III) complexes are about 24 kcal. On the basis of this value and the calculated values of Basolo and Pearson mentioned above the S_N1 mechanism with a square pyramid transition state structure remains the only possibility out of those considered. The value range 6 - 94 kcal. for this mechanism represents the extreme cases where the vacated position is either completely or not at all occupied by water, so that the value of 24 kcal. seems to suggest that water is involved to some extent in the transition state structure. The question whether a specific water molecule is involved in the transition state or the solvation sheath in general, however, is merely another way of asking whether the reaction should be called S_N1 or S_N2 .

Other indirect methods of approach toward the understanding of the aquation mechanism have been studies on the effect of increased chelation (13), the nature of the leaving group (14), the net charge on the complex ion (15), steric hindrance (16), displacement of the bonding electrons (17), and the nucleophilicity of attacking groups (18). In general the results are somewhat ambiguous in terms of being able to decide upon the exact mechanism involved. Ingold (19) has shown that by changing the nature of one of the non-labile ligands it has been possible to change the mechanism of the reaction, and has correlated the polar effect of the orienting substituent with the change in mechanism (20).

Evidence for the participation of water in the rate determining step has been found (21), (22), (23). Adamson and Basolo (21), on the basis of deuterium isotope effect measurements on the rate of aquation, proposed

an intermediate structure containing hydrogen bond bridges between ligand and solvent. Adamson (22) again interpreted solvolysis data for Reinecke's salt in terms of a hydrogen bonded intermediate involving the solvent. Tobe (23) interpreted his results to show that hydrogen bonding between the incoming ligand water and the outgoing ligand was responsible in some part for the lowering of the activation energy of the aquation reaction.

The aquation mechanism in most cases seems to show characteristics of both limiting pathways, S_N1 and S_N2 . The mechanism appears to involve solvent participation in the rate determining step, and it is the degree of solvent participation which corresponds to the mechanism being more S_N1 or more S_N2 in character.

Electrolyte Effects

It has been known for more than half a century that kinetic measurements in ionic solutions often yield results which are inexplicable on the basis of the classical theory of Arrhenius and van't Hoff (24). One such phenomenon which remained for some time inexplicable, was the effect of the presence of neutral salts on the measured rate constants. Brønsted (25) was the first to formulate the effect of a neutral salt on the rate constant. Other major contributions to the theory were made by Debye and Huckel (26), Bjerrum (27), and Christiansen (28). A complete review of the theory was given by La Mer (68).

The basis of the theory is that the reaction rate depends upon the relative values of the chemical potentials of the initial and final states of the systems, i.e. on the activities rather than the concentrations of the species involved. As a result three classes of electrolyte effects can be distinguished:

- (1) The primary salt effect, which involves the use of activities rather than concentrations of the reacting ions in the kinetic expressions.
- (2) The secondary salt effect, which is due to the shift in the degree of dissociation of a reactant weak electrolyte.
- (3) Generalized acid - base catalysis, which differs from the primary and secondary salt effects in that it is not a "neutral" electrolyte effect.

On the following pages the electrolyte effect on the rate constant is illustrated through the derivation of the general rate expressions for the S_N1 and the S_N2 mechanisms in terms of activities. The symbols used are defined as:

M - and electrophilic positive complex ion (no charges will be shown)

A - a nucleophilic ligand (no charges will be shown)

W - water

() - molar concentration

// - activity

y - molar activity coefficient

k_1, k_2, k_3 - rate constants

k_0 - absolute rate constant, independent of electrolyte concentration

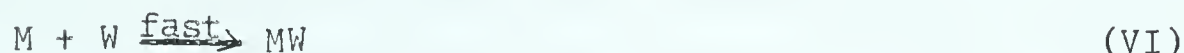
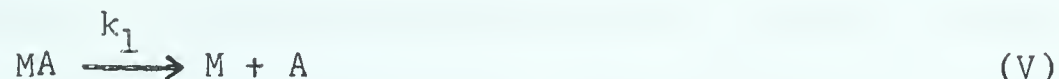
w, m - initial concentrations of W and MA

x - the reaction variable

The rate expressions are to be used with the experimental data obtained. The initial concentration of the complex ion used is of the order 10^{-3} M and the concentration of inert electrolyte in each experiment was at least 0.1 M, so that for this work y_{MX} and y_W are constant during the procedure of the reaction.

The S_N1 Mechanism

The S_N1 mechanism has a unimolecular dissociation as the rate determining step, and can be written as follows:



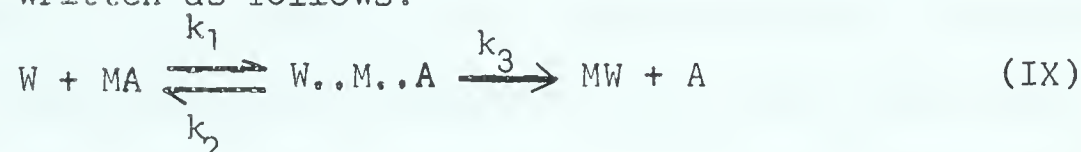
The integrated rate expression is then derived as follows:

$$\frac{dx}{dt} = k_1/MA/ = k_0 y_{MX}(MA) = k_0 y_{MX}(m-x) \quad (VII)$$

$$\ln \frac{m}{m-x} = y_{MX} k_0 t \quad (VIII)$$

The S_N2 Mechanism

The S_N2 mechanism has a bimolecular displacement as the rate determining step, and is written as follows:



The integrated rate expression for this is derived as follows:

$$\frac{dx}{dt} = \frac{k_1 k_3}{k_2 + k_3} /W//MA/ = k_0 y_{MX} y_W (W)(MA) = k_0 y_{MX} y_W (w-x)(m-x) \quad (X)$$

$$\frac{1}{w-m} \ln \left(\frac{m(w-x)}{w(m-x)} \right) = y_{MX} y_W k_0 t \quad (XI)$$

However, since both m and x have 10⁻³ M as their upper value, they are negligible quantities with respect to w, so that (w - m) = w and (w - x)/w = 1. The rate expression can then be simplified to:

$$\frac{1}{w} \ln \left(\frac{m}{m-x} \right) = y_{MX} y_W k_0 t \quad (XII)$$

$$\ln \left(\frac{m}{m-x} \right) = y_{MX} /W/k_0 t \quad (XIII)$$

The S_N2 rate expression therefore simplifies to the S_N1 rate expression, with the important difference, that the pseudo first order rate constant k now depends on the activity of water:

$$\text{For } S_N1: k = y_{MX} k_0 \quad (\text{XIV})$$

$$\text{For } S_N2: k = y_{MX} k_0 / W \quad (\text{XV})$$

The aquation of bromopentamminechromium(III) cation has been suggested to proceed by a "solvent assisted S_N1 mechanism" (69), in which the rate determining step, the unimolecular dissociation, involves participation of the solvent sheath. This would mean that the pseudo first order rate constant would vary with the n^{th} power of the water activity:

$$k = y_{MX} k_0 / W^n \quad (\text{XVI})$$

This rate expression represents all three of the mechanisms discussed; for the S_N1 mechanism $n = 0$, for the S_N2 mechanism $n = 1$, while for the solvent assisted S_N1 mechanism $n \neq 0$. The value of n may be obtained from equation (XVI) by rearranging and taking logs, as in equation (XVII), since then a plot of $\log(k/y_{MX} k_0)$ vs. \log/W should yield a straight line plot with slope = n .

$$\log(k/y_{MX} k_0) = n \log/W \quad (\text{XVII})$$

The construction of such plots requires, in addition to the rate data, a knowledge of the activity coefficient of the complex and the activity of water at each concentration of electrolyte studied. Water activities are best calculated from the experimentally measured osmotic coefficient (70), as is shown in a later section (page 37).

In very dilute solutions the activity coefficient of the complex cation could probably be approximated with an equation such as the Extended Debye - Huckel Equation (71), shown below (XVIII).

$$-\log y = \frac{0.51 |Z|^2 \sqrt{u}}{1 + 0.33 a \sqrt{u}} \quad (\text{XVIII})$$

It has been shown, however, (72) that in the limiting case where a very small amount of one electrolyte is present along with a large excess of another electrolyte, the mean activity coefficient of the electrolyte in excess is

not altered significantly, while the activity coefficient of the dilute species has a value intermediate to those of the separate electrolytes at the same total concentration. Thus, in the presence of a large excess of inert electrolyte the activity coefficient of the cation will depend on the activity rather than the concentration of the inert electrolyte. The extent of this dependence cannot at present be estimated quantitatively, and even the prediction of qualitative trends is hazardous.

In this thesis an attempt is made to show that the decrease in rate constant with increasing hydrogen ion concentration below $\text{pH}=1$ for the aquation of bromopentamminechromium(III) cation is a general electrolyte effect and to explain this electrolyte effect in terms of present day knowledge of electrolyte behaviour in concentrated solutions.

II EXPERIMENTAL

Preparation of $[\text{Cr}(\text{NH}_3)_5\text{Br}]\text{Br}_2$

Bromopentamminechromium(III) bromide was prepared from the aquopentamminechromium(III) nitrate ammonium nitrate double salt according to the method described by M. Mori (29). This double salt was obtained by reacting potassium chromium(III) sulphate with a mixture of aqueous ammonia and ammonium nitrate at 60° . Air was passed through the resulting purple sludge to remove the excess ammonia. A measured excess of concentrated nitric acid was carefully added to the solution with the temperature of the solution being kept below 30° by cooling in an ice/water mixture. On cooling orange crystals of $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}](\text{NO}_3)_3 \cdot \text{NH}_4\text{NO}_3$ separated out. These were filtered, washed with 95% ethanol, and air dried.

A 1.0M solution of aquopentamminechromium(III) nitrate ammonium nitrate in 4 M ammonia was allowed to react with 48% HBr, and the reaction mixture allowed to digest on a steambath for 30 minutes. Pink crystals of bromopentamminechromium(III) bromide separated out. These were filtered, washed with 95% ethanol, and air dried.

The pink crystalline product was observed to have a polarographic half-wave potential of -0.6 volts, which agrees with the reported value for the bromopentamminechromium(III) complex (30). No wave was initially observable at -0.9 volts, where the aquopentamminechromium(III) complex is reduced. Hence the concentration of the aquopentamminechromium(III) complex as an initial impurity was negligible for the purpose of this work.

Polarography of Chromium Complexes

Figure 1 shows a series of polarograms obtained during the acid hydrolysis of a solution of 10^{-3} M bromopentamminechromium(III) bromide in 0.1 M perchloric acid at 25°. Three of the kinetically important species present gave polarographic waves, each of which could be used to follow the reaction.

The oxidation of bromide ion gives a wave at 0.15 volts, so that the appearance of bromide ion could be followed. The one electron reduction of the chromium complexes gives rise to the other two waves. The bromopentamminechromium(III) cation is reduced at about -0.6 volts, while the aquopentamminechromium(III) cation is reduced at about -0.9 volts. Both the disappearance of the bromo complex and the appearance of the aquo complex could therefore be followed. No wave due to the reduction of any other chromium species was observed.

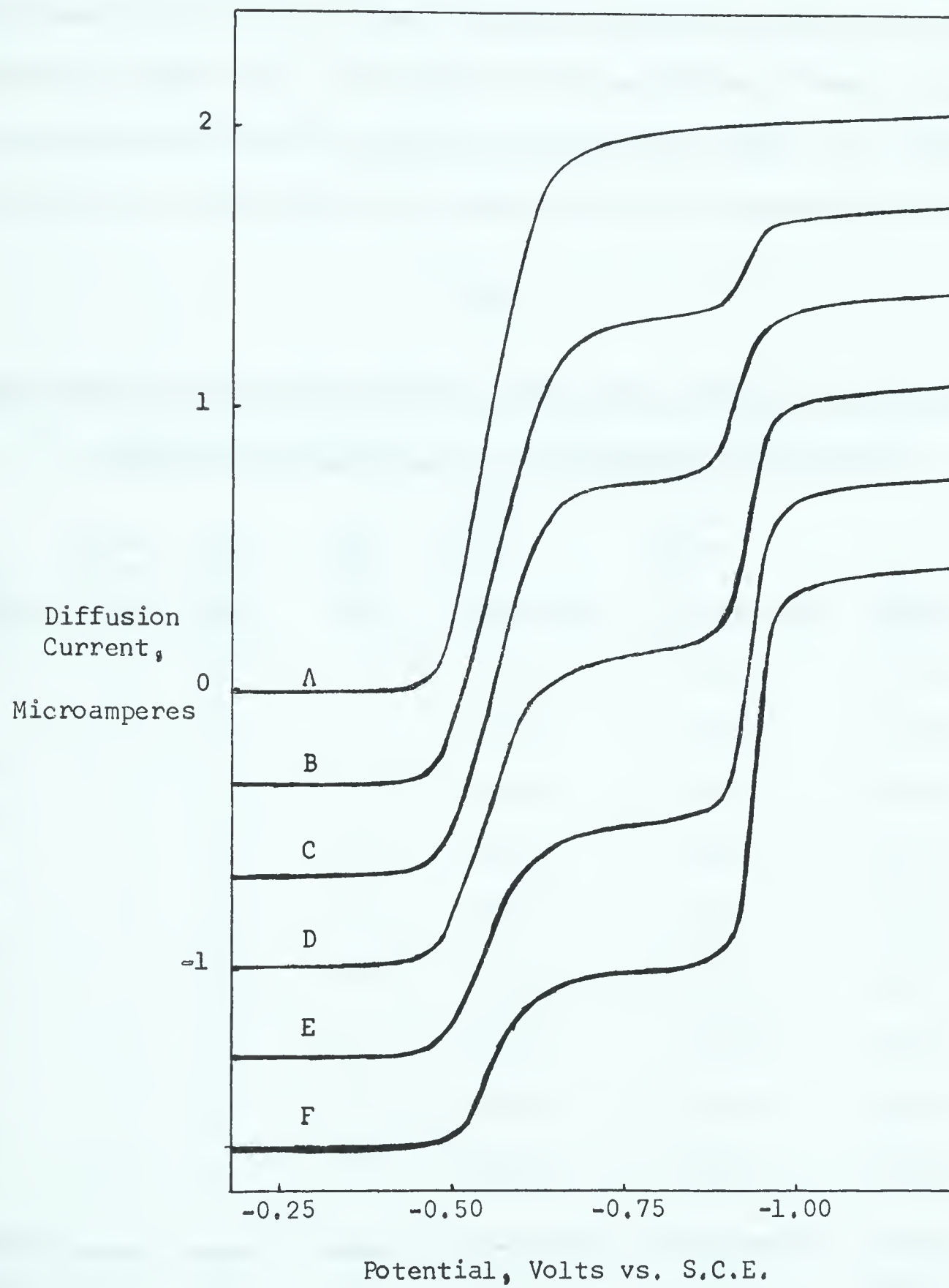
Several factors influenced the choice of the bromo complex wave as the most desirable for following the reaction.

- (I) Bromide ion was present initially as the anion of the complex. The contribution of the bromide ion liberated during the reaction to the total wave height would therefore be less than one third, resulting in a loss of precision. The salt could have been converted to the less stable perchlorate salt to eliminate this objection.
- (II) At high electrolyte concentration, especially when the electrolyte was perchloric acid, the shift of the hydrogen discharge wave to more positive potential distorted or obscured the aquo complex wave, making its analysis impossible.

Figure 1

Schematic diagrams of polarograms obtained during
the aquation of $\text{Cr}(\text{NH}_3)_5\text{Br}^{++}$ at 25.0° in 0.1 M
perchloric acid

- A. 0 mins.
- B. 20 mins.
- C. 50 mins.
- D. 90 mins.
- E. 130 mins.
- F. 180 mins.



The wave obtained for the bromo complex is non-ideal, in that the slope of the diffusion current plateau does not lie parallel to the baseline. Additionally, a slight variation in such wave characteristics as the half-wave potential and the total wave height were observed even for consecutive samples of a single run. An example of the variation of some of these wave characteristics for a typical run are given in table I in order to demonstrate the reproducibility possible with this method of analysis.

TABLE I

POLAROGRAPHIC WAVE CHARACTERISTICS DURING THE AQUATION OF BROMOPENTAMMINE-CHROMIUM(III) BROMIDE IN 0.1 M PERCHLORIC ACID AT 25°.

<u>t,</u> <u>minutes</u>	<u>base-</u> <u>line</u> <u>slope</u>	<u>bromo</u> <u>plat.</u> <u>slope</u>	<u>aquo</u> <u>plat.</u> <u>slope</u>	<u>total</u> <u>wave</u> <u>ht. at</u> <u>-0.9 v. (mm)</u>	<u>total</u> <u>wave</u> <u>ht. at</u> <u>-1.0 v. (mm)</u>	<u>E 1/2</u> <u>bromo</u>	<u>E 1/2</u> <u>aquo</u>
0	0°	13°	2°	114.0	115.0	-.618	-.918
20	0	12	3	115.7	116.9	-.608	-.898
50	0	11 ₅	3	116.9	118.5	-.606	-.895
70	0	12	3	117.2	118.6	-.607	-.892
90	0	12 ₅	6	115.7	118.5	-.604	-.897
110	0	14 ₅	4	115.3	117.3	-.614	-.903
130	0	14	4	115.6	117.9	-.598	-.895
160	0	12	4	115.0	117.0	-.603	-.898
180	0	11	6	111.1	114.5	-.599	-.893
<u>medians</u>	<u>0</u>	<u>12</u>	<u>4</u>	<u>115.6</u>	<u>117.1</u>	<u>-.606</u>	<u>-.897</u>

An indication of the reproducibility of the wave height measurements is given by the probable deviation of the collective total wave height data given in table I: the probable deviation is 1.0 mm or slightly less than 1%.

For non-ideal polarographic waves the response between wave height and concentration is not necessarily linear (31). Therefore, a series of known concentrations of bromo complex were polarographed by adding a weighed amount of complex to a measured amount of liquid containing both the background electrolyte and the maximum suppressor. In order to keep a variation to a negligible minimum the polarograms were run immediately upon solution of the complex and at 0°. The wave height was measured both at the half-wave potential of the bromo complex, and at a constant voltage on the bromo wave plateau (-0.77 v.). The results are shown in table II.

TABLE II

CONCENTRATION VS. WAVE HEIGHT FOR KNOWN BROMOPENTAMMINECHROMIUM(III)

BROMIDE CONCENTRATIONS

$M \times 10^{-3}$	at -0.6v. id.mm.	$\frac{id}{M \times 10^{-3}}$	at -0.77v. id.mm.	$\frac{id}{M \times 10^{-3}}$
1.500	164.0	109	172.2	115
1.129	129.1	114	132.6	117
1.115	126.3	114	129.7	116
0.837	88.2	106	94.9	113
0.498	54.0	108	56.5	113
0.328	39.1	118	41.8	127
0.164	11.7	71	13.4	80
0.058	5.0	86	7.1	122

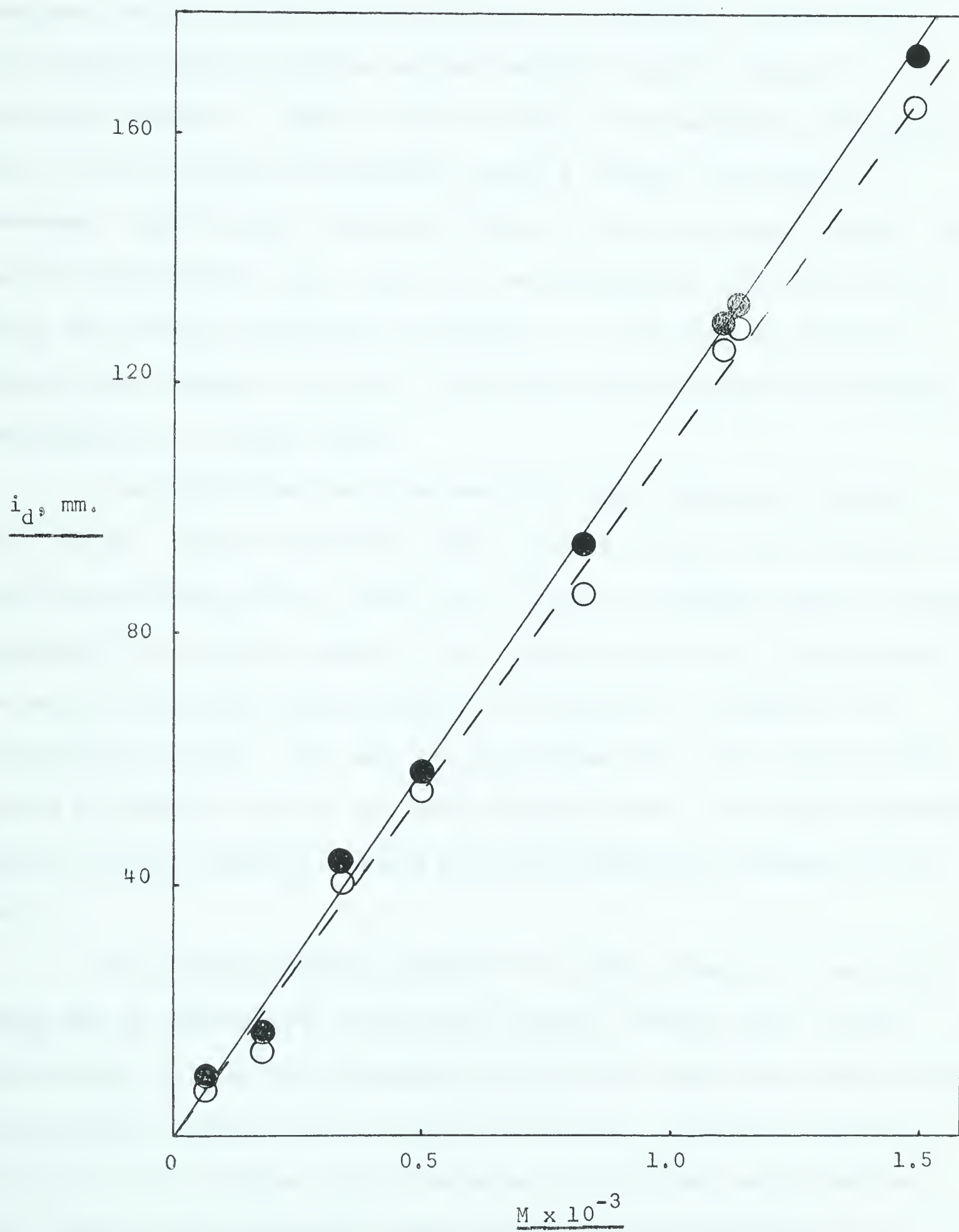
The consistency of the $i_d/M \times 10^{-3}$ ratio in both cases indicates, that a linear response between concentration and wave height may be assumed at concentrations of 5×10^{-4} and higher, the probable deviation in this region being about 2%. At more dilute concentrations linearity is obeyed as well, but the difficulty in measuring the small wave heights causes a large percentage error. The data of table II are used to illustrate linearity in figure 2.

Figure 2

WAVE HEIGHT VS. CONCENTRATION OF BROMOPENTAMMINECHROMIUM(III) BROMIDE

Solid line and points - wave height measured at -0.77 volts.

Open line and points - wave height measured at -0.60 volts.



Technique of Polarographic Measurements

The polarograph is made up of six major components. The central component is the electrolysis cell which, when assembled, contains both the dropping mercury electrode and the saturated calomel reference electrode terminals. Figure 3 shows a sketch of the assembled polarographic cell. The electrodes are connected through a voltage scan system to a recorder. Additionally, a nitrogen bubbler is used for oxygen removal. The use of a polarographic cell such as the one constructed by Harris (32), in which the reference electrode is connected to the solution by means of a flexible salt bridge, has greatly facilitated making repeated polarographic measurements on a single system.

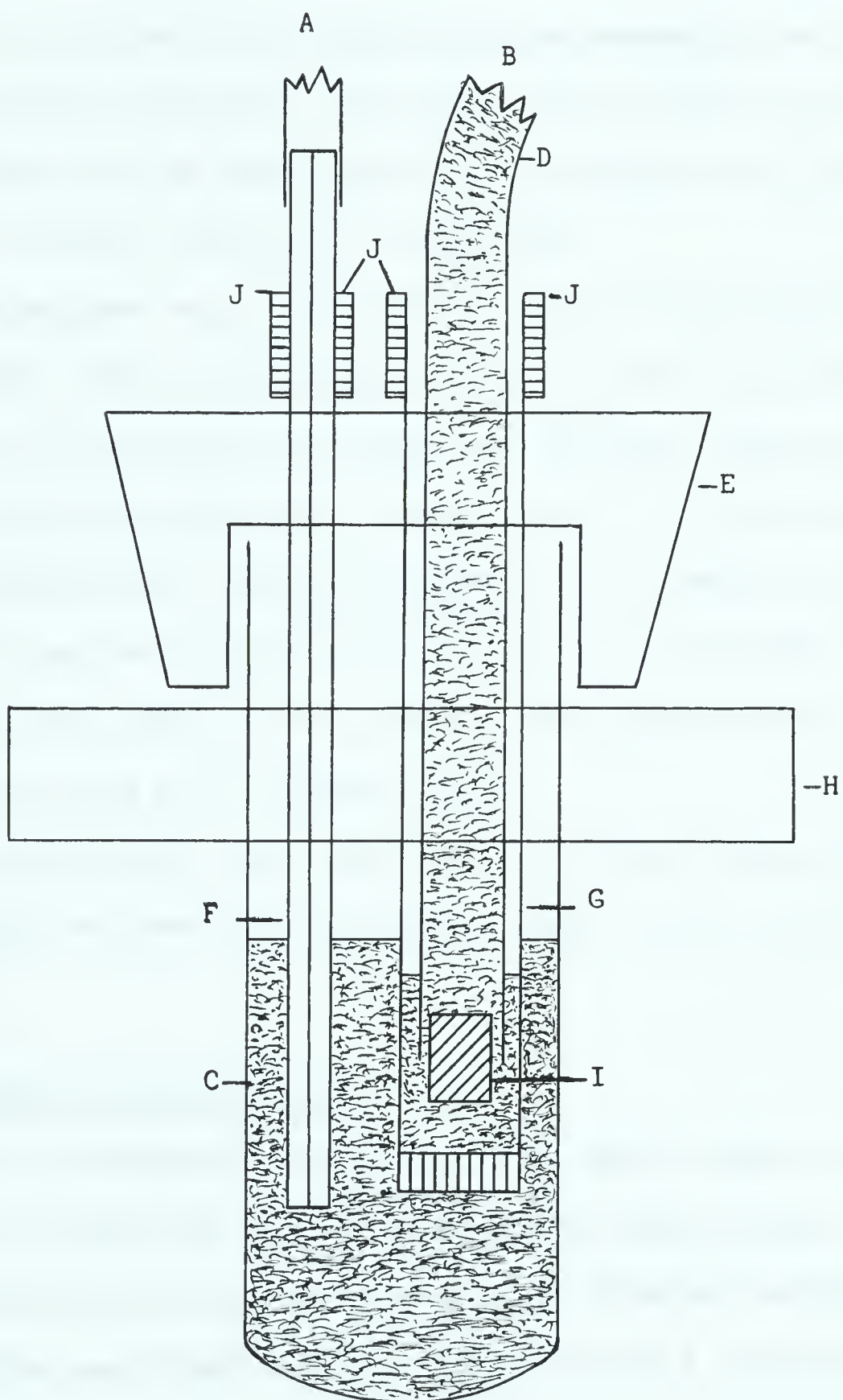
The electrolysis cell was made from glass tubing and measured 25 x 100 mm. The cell was fitted with a partially hollow rubber stopper E, which was provided with two holes, one to admit the dropping mercury electrode capillary F, the other to admit a fine sintered glass tube G, which served to provide electrical contact between the flexible salt bridge and the electrolysis solution. The cell was also fitted with a cork disc H, which served to position the cell in a dewar flask ice bath. All these components could be readily removed, allowing for rapid assembly and disassembly of the cell.

The nitrogen bubbler consisted of a finely drawn out tube which, along with an exhaust tube, were passed through a stopper which fit the electrolysis cell, so that deaerating could be done immediately prior to the polarographic analysis and in a separate ice bath. The bubbler tube was connected to the nitrogen supply through a 12 foot copper coil which was also placed in the ice bath to allow pre-cooling of the nitrogen to 0°.

Figure 3

The Polarographic Cell

- A. Dropping mercury electrode.
- B. To saturated calomel electrode cell.
- C. Glass electrolysis cell.
- D. Flexible salt bridge.
- E. 2 hole rubber stopper.
- F. Electrode capillary.
- G. Glass tube with sintered glass plug.
- H. Cork disc support.
- I. Agar plug.
- J. Supports for positioning electrodes.



The saturated calomel electrode was prepared in a 25 ml. distilling flask with a flexible side-arm connection D. Electrical contact between the electrode solution and the sample solution was made through an agar plug I, which was fitted in the end of the rubber side-arm connection, as in figure 3.

The recorder and voltage scan system used for most of the polarographic measurements was the Leeds and Northrup Speedomax G, but for a few kinetic runs the Metrohm Polarecord E 261 was used.

All polarograms were recorded at 0°, with the electrolyte cell immersed in a dewar flask containing an ice/water mixture. Recording of the polarograms at this temperature offered the important advantage, that the aquation reaction was effectively quenched at 0°. The quenching time was kept to a minimum by the immediate immersion of the sample aliquot in an ice/water bath and the bubbling through of pre-cooled nitrogen. An estimated error of the reaction time, based on the reproducibility of the cooling procedure, would be 1/2 minute or less.

The polarographic setup described above allowed rapid, continuous analysis of samples and was therefore ideally suited to this kinetic investigation.

Kinetic Measurements by Polarography

Since a polarographic analysis could be made in about 5 minutes, it was possible to follow six separate kinetic runs simultaneously. The six reaction mixtures were prepared at five minute intervals and aliquots were withdrawn from each flask every half hour, so that a polarogram was obtained every five minutes.

The reaction mixtures were made up in 50 ml. volumetric flasks, which were wrapped in aluminum foil to eliminate photochemical reactions (33).

The flask was partially filled with water and the required perchlorate electrolyte reagent, and placed in a Colara Ultrathermostat water bath, which monitored the temperature to $25.0^{\circ} \pm 0.05^{\circ}$. After the solution had attained bath temperature a weighed amount of bromopentamminechromium(III) bromide was added to make the final concentration of complex about $10^{-3}M$. Bath-temperature water was added to make the solution up to volume and the flask was shaken briefly to dissolve the complex.

A 5 ml. aliquot was pipetted into an electrolysis cell which contained one drop of 1/2% gelatin solution. The gelatin effectively served as the maximum suppressor. The cell was immediately placed in an ice/water bath and pre-cooled nitrogen was bubbled through the solution to remove the dissolved oxygen. Oxygen was effectively removed in less than 2 minutes. The rapid bubbling action insured rapid cooling of the sample as well.

After deaeration the cell was placed in the second ice/water bath with the rubber stopper and cork disc attached. Suction was applied to the sintered glass tube to draw up some of the solution, so that on insertion of the flexible salt bridge the electrical circuit would be completed. The electrodes were then inserted into the cell and the polarogram recorded, while another sample was similarly prepared.

The half life of the fastest reaction studied was about 1 1/2 hours and each run was usually followed for a period of two half lives. In all the polarographic analyses the perchlorate electrolyte served as the background electrolyte for the polarographic process as well.

Determination of the Rate Constant

The acid hydrolysis of the bromopentamminechromium(III) cation is a pseudo first order reaction. The specific rate constant, k , can be expressed in the form of equation (XIX).

$$k = \frac{2.303}{t} \log \frac{c_0}{c} \quad (\text{XIX})$$

where c_0 is the initial concentration of the reactant, and c is the concentration of the reactant at any time t . According to the Ilkovic equation (34) the measured diffusion current is linearly proportional to the concentration of the species being reduced, and this has been affirmed experimentally in the case of the bromo complex under consideration (35). The specific rate constant can therefore be obtained from diffusion current measurements by application of equation (XX).

$$k = \frac{2.303}{t} \log \frac{i_{d_0}}{i_d}, \quad (\text{XX})$$

where i_{d_0} is the diffusion current at zero time, and i_d is the diffusion current at any time t . A plot of $-\log i_d$ against time should give a straight line, with the rate constant being calculated from the slope by equation (XXI).

$$k = 2.303 \times \text{slope}, \quad (\text{XXI})$$

A typical set of diffusion current measurements is given in table III, and the corresponding values of $-\log i_d$ are plotted in figure 4. The data are those obtained from the analysis of the polarographic waves shown in figure 1.

TABLE III

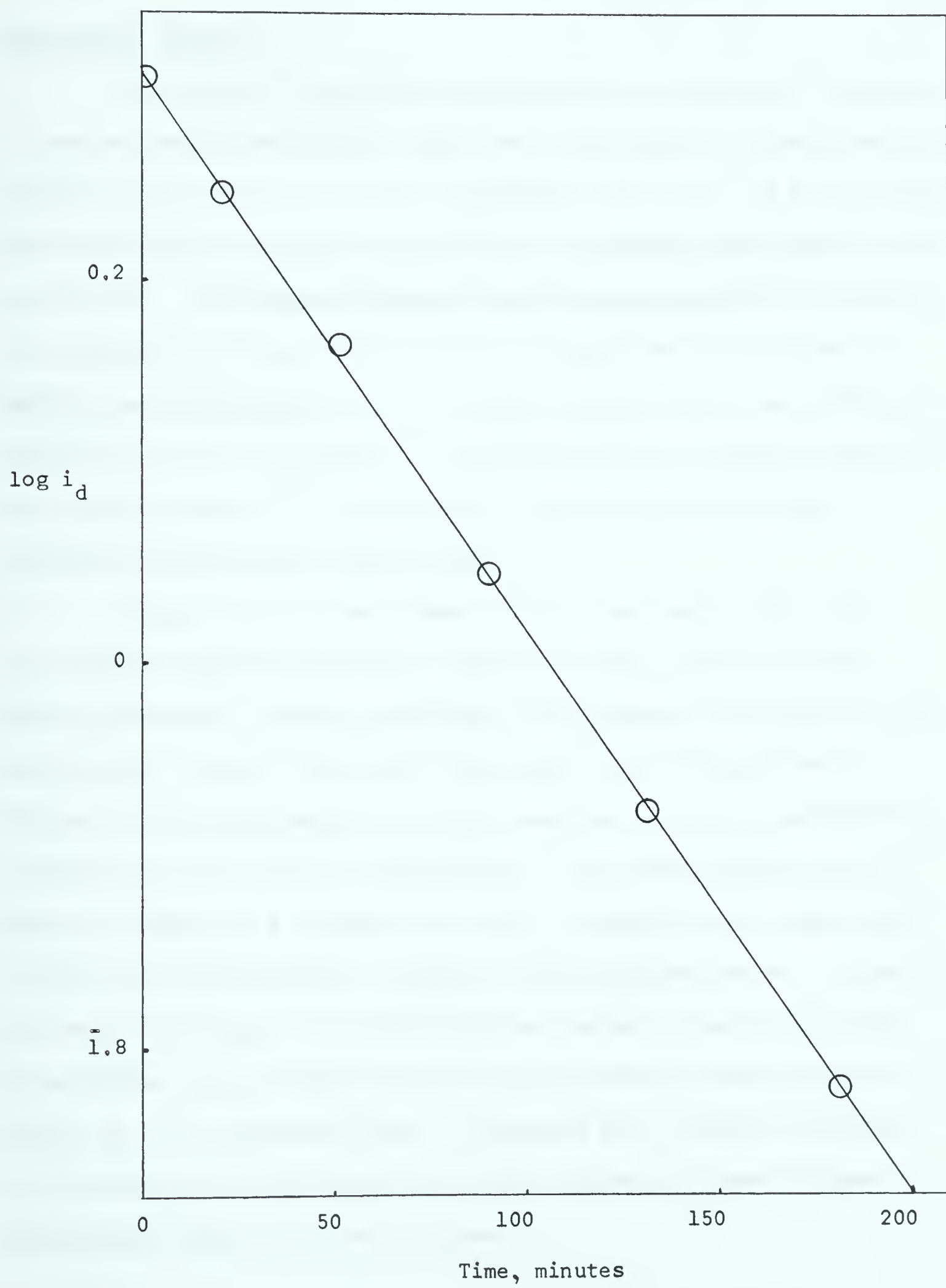
DIFFUSION CURRENT READINGS DURING THE AQUATION OF $\text{Cr}(\text{NH}_3)_5\text{Br}^{++}$

AT 25.0° IN 0.1 M PERCHLORIC ACID

<u>Time minutes</u>	<u>Diffusion current (i_d) microA.</u>	<u>$\log i_d$</u>
0	2.016	0.3045
20	1.758	0.2450
50	1.474	0.1685
90	1.120	0.0492
130	0.832	$\overline{1}.9201$
180	0.598	$\overline{1}.7767$

Figure 4

Plot of log diffusion current against time for
aquation of $\text{Cr}(\text{NH}_3)_5\text{Br}^{++}$ at 25.0° in 0.1 M
perchloric acid



III HIGH CONCENTRATION SALT EFFECTS ON THE AQUATION REACTION

Experimental Results

The effect of electrolyte concentration on the rate of aquation of bromopentamminechromium(III) cation was investigated for concentrations ranging from 0.1 M up to 3.5 M for perchloric acid, up to 4.9 M for sodium perchlorate, and up to 2.0 M for lithium and magnesium perchlorates as the electrolytes. All reaction mixtures containing perchlorate species other than perchloric acid were made 0.1 M in perchloric acid. All rates of reaction were investigated at 25.0°, using varying amounts and species of perchlorates as the electrolyte. The concentration of chromium complex in all cases was about 10^{-3} M, so that its contribution to the total electrolyte concentration was negligible.

Figures 5, 6, 7, and 8 show plots of the pseudo first order rate constant against electrolyte concentration for perchloric acid, sodium perchlorate, lithium perchlorate, and magnesium perchlorate as the electrolyte. The data from which these plots were constructed were obtained by the polarographic procedure described previously and are shown in tables IV, V, VI, and VII respectively. The values reported are, in general, averages of a minimum of two runs, although in some cases three or four runs were necessary to obtain a self-consistent value. For each electrolyte the value of the limiting rate constant at zero electrolyte concentration (k_0) was taken as the value obtained by hydrolyzing the complex in 0.1 M perchloric acid. A composite plot, showing the effect on the hydrolysis rate of each of the four electrolytes over the same concentration range, is shown in figure 9.

TABLE IV

EFFECT OF PERCHLORIC ACID UPON THE RATE OF AQUATION OF
BROMOPENTAMMINECHROMIUM(III) CATION AT 25.0°

<u>Electrolyte Concentration</u>	<u>$k \times 10^3 \text{ min}^{-1}$</u>	<u>$\log (k \times 10^3)$</u>
0.06	7.0	.84 ₅
0.10	6.9	.84
0.20	6.3	.80
0.30	6.1	.78 ₅
0.50	5.8	.76 ₅
0.60	5.2	.71 ₅
1.00	4.6	.66 ₅
1.20	4.4	.64 ₅
2.10	3.1	.49
3.50	2.5	.40

TABLE V

EFFECT OF SODIUM PERCHLORATE UPON THE RATE OF AQUATION
OF BROMOPENTAMMINECHROMIUM(III) CATION AT 25.0°

<u>Salt Concentration</u>	<u>$k \times 10^3 \text{ min}^{-1}$</u>	<u>$\log (k \times 10^3)$</u>
	6.9	.84
0.05	6.8	.83
0.10	6.5	.81
0.25	6.1	.78 ₅
0.40	5.7	.75 ₅
0.50	5.5	.74
0.63	5.3	.72 ₅
0.70	5.2	.71 ₅
0.90	5.0	.70
1.00	4.9	.69
1.20	4.7	.67
1.50	4.4	.64 ₅
1.70	4.2	.62 ₅
1.90	4.2	.62 ₅
2.00	4.1	.61 ₅
2.50	3.8	.58
3.00	3.6	.55 ₅
3.50	3.3	.52
4.00	3.0	.47 ₅
4.90	2.6	.41 ₅

TABLE VI

EFFECT OF LITHIUM PERCHLORATE UPON THE RATE OF AQUATION
OF BROMOPENTAMMINECHROMIUM(III) CATION AT 25.0°

<u>Salt concentration</u>	<u>$k \times 10^3 \text{ min}^{-1}$</u>	<u>$\log (k \times 10^3)$</u>
0.00	6.9	.84
0.10	6.6	.82
0.20	6.3	.80
0.40	6.0	.78
0.50	5.8	.76 ₅
0.60	5.6	.75
0.90	5.0	.70
1.00	5.0	.70
1.20	4.6	.66 ₅
1.50	4.2	.62 ₅
2.00	3.7	.57

TABLE VII

EFFECT OF MAGNESIUM PERCHLORATE UPON THE RATE OF AQUATION
OF BROMOPENTAMMINECHROMIUM(III) CATION AT 25.0°

Salt concentration	$k \times 10^3 \text{ min}^{-1}$	$\log (k \times 10^3)$
0.00	6.9	.84
0.05	6.5	.81 ₅
0.10	6.3	.80
0.20	6.0	.78
0.30	5.8	.76 ₅
0.50	5.2	.71 ₅
0.80	4.7	.67
1.00	4.4	.64 ₅
1.60	3.2	.51
2.00	2.0	.30

Figure 5

Effect of perchloric acid on the rate of aquation of
bromopentamminechromium(III) cation at 25.0°.

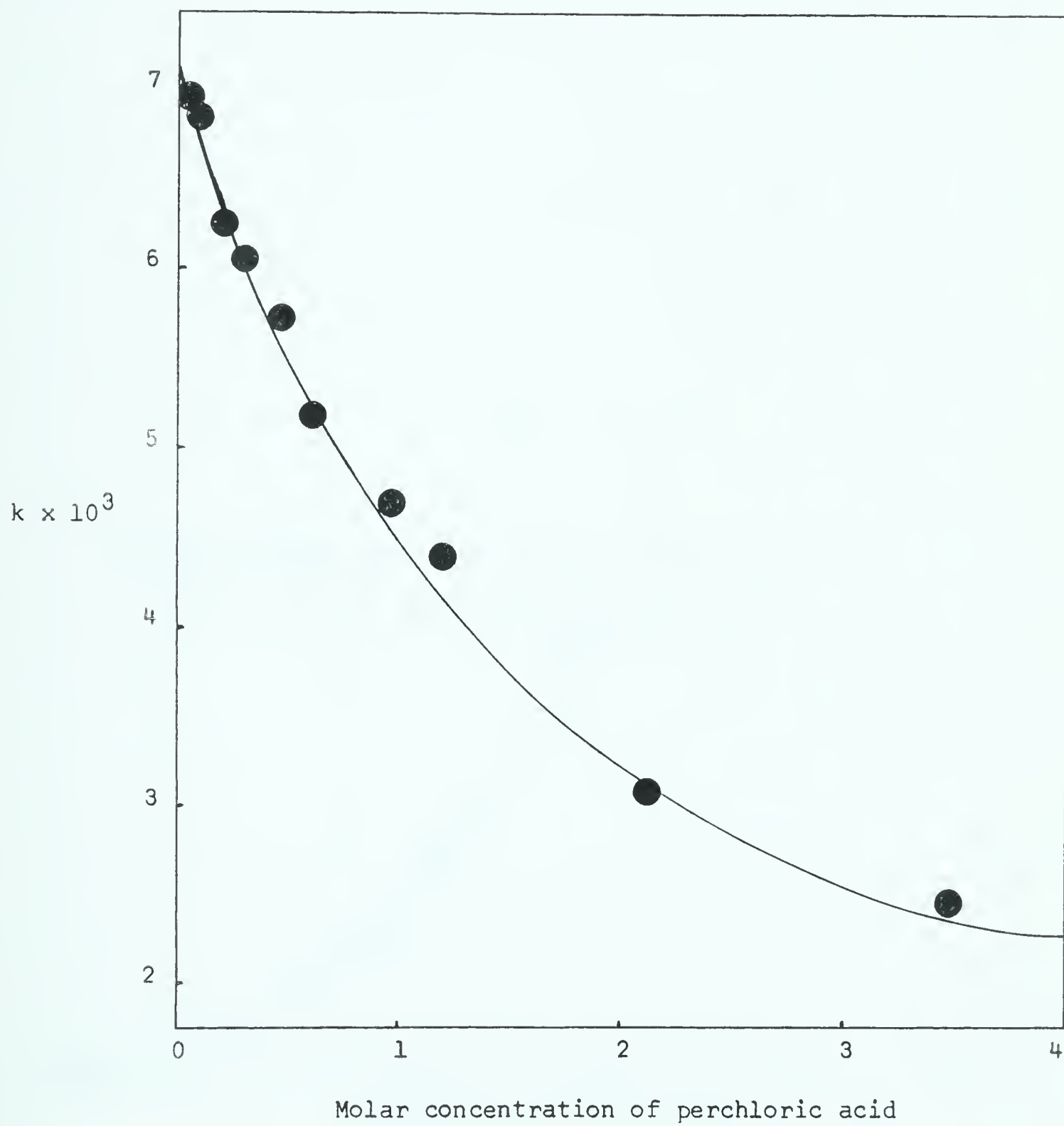


Figure 6

Effect of sodium perchlorate on the rate of aquation
of bromopentamminechromium(III) cation at 25.0°.

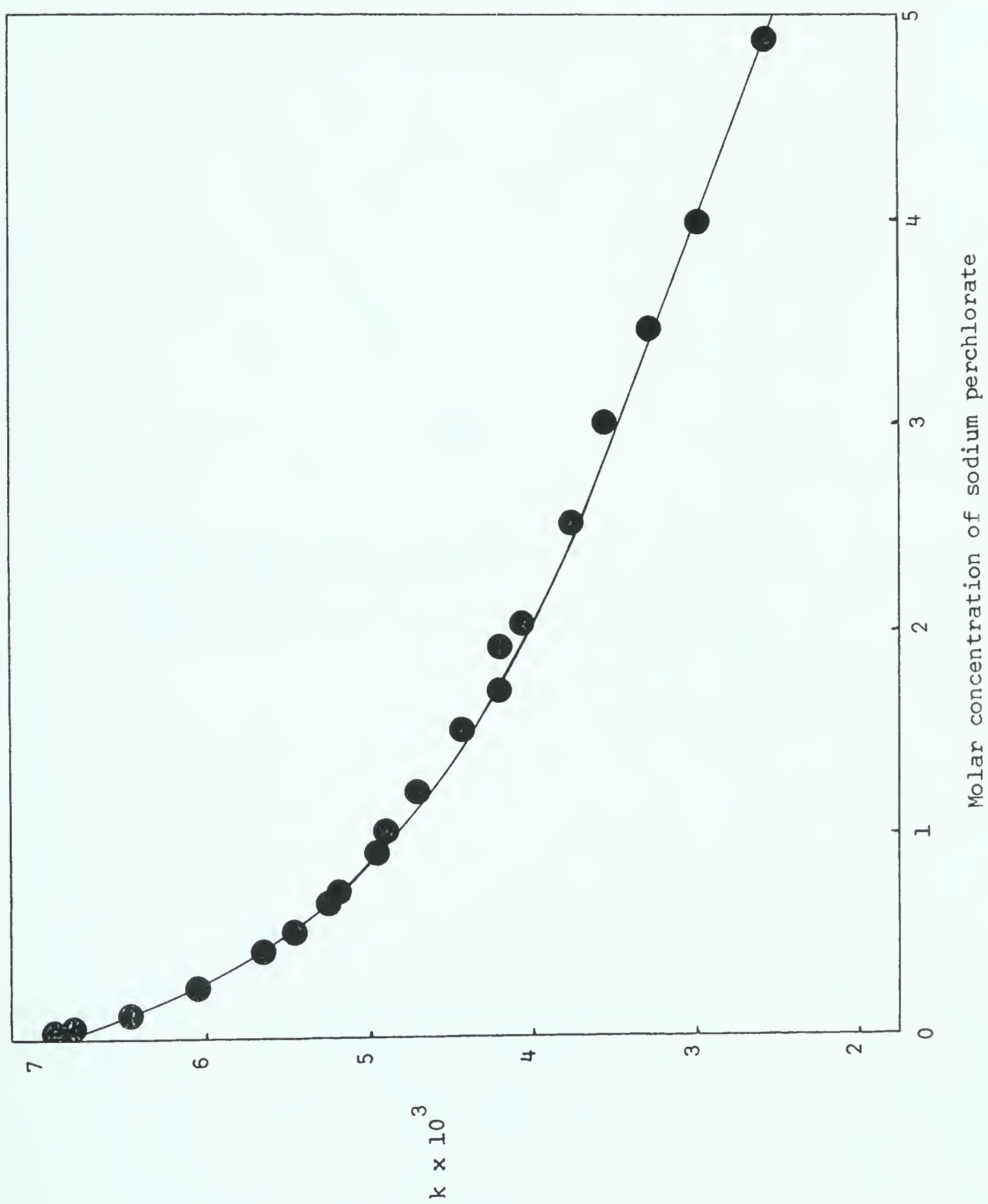


Figure 7

Effect of lithium perchlorate on the rate of aquation of
bromopentamminechromium(III) cation at 25.0°.

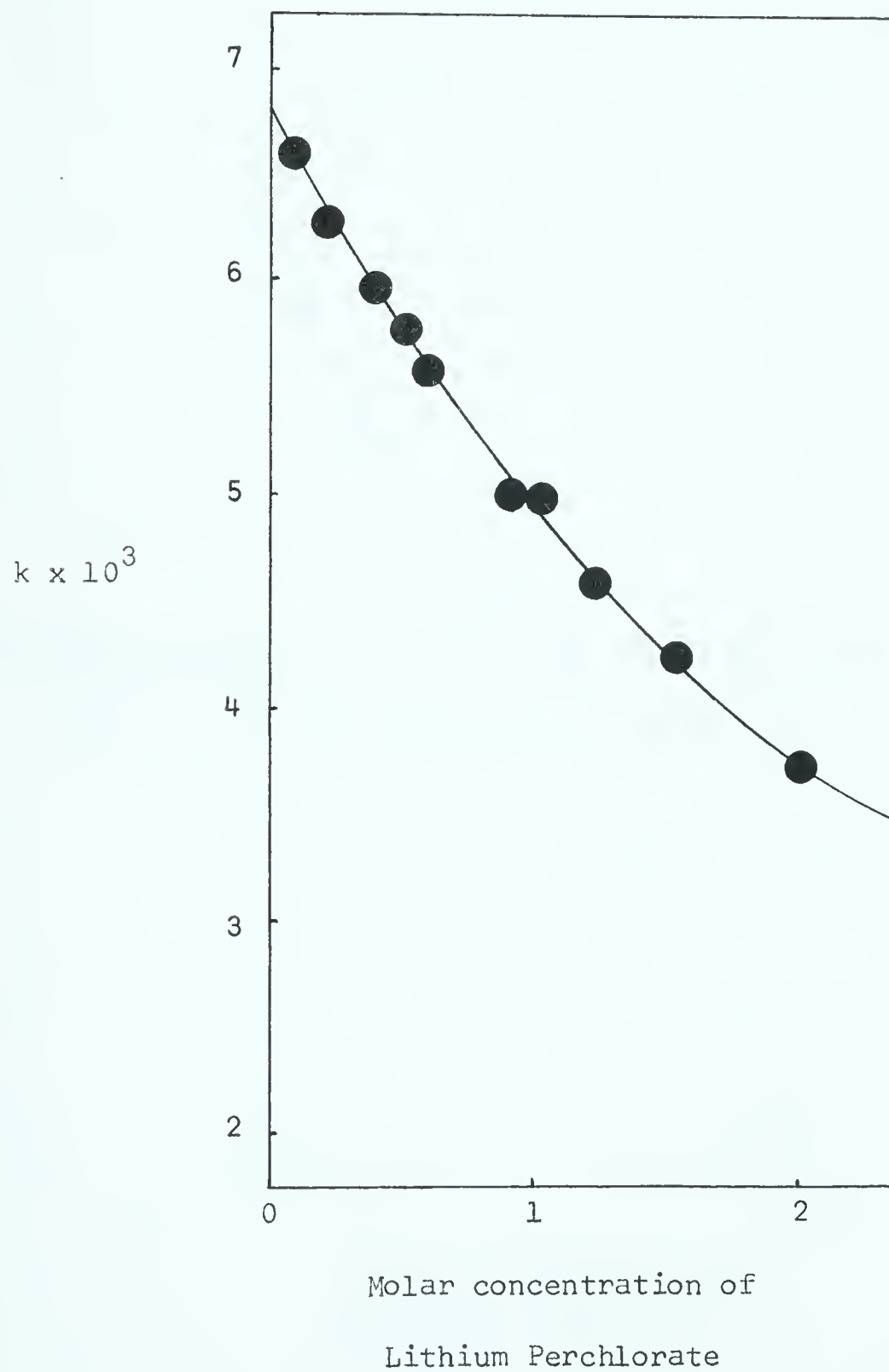


Figure 8

Effect of magnesium perchlorate on the rate of aquation
of bromopentamminechromium(III) cation at 25.0°.

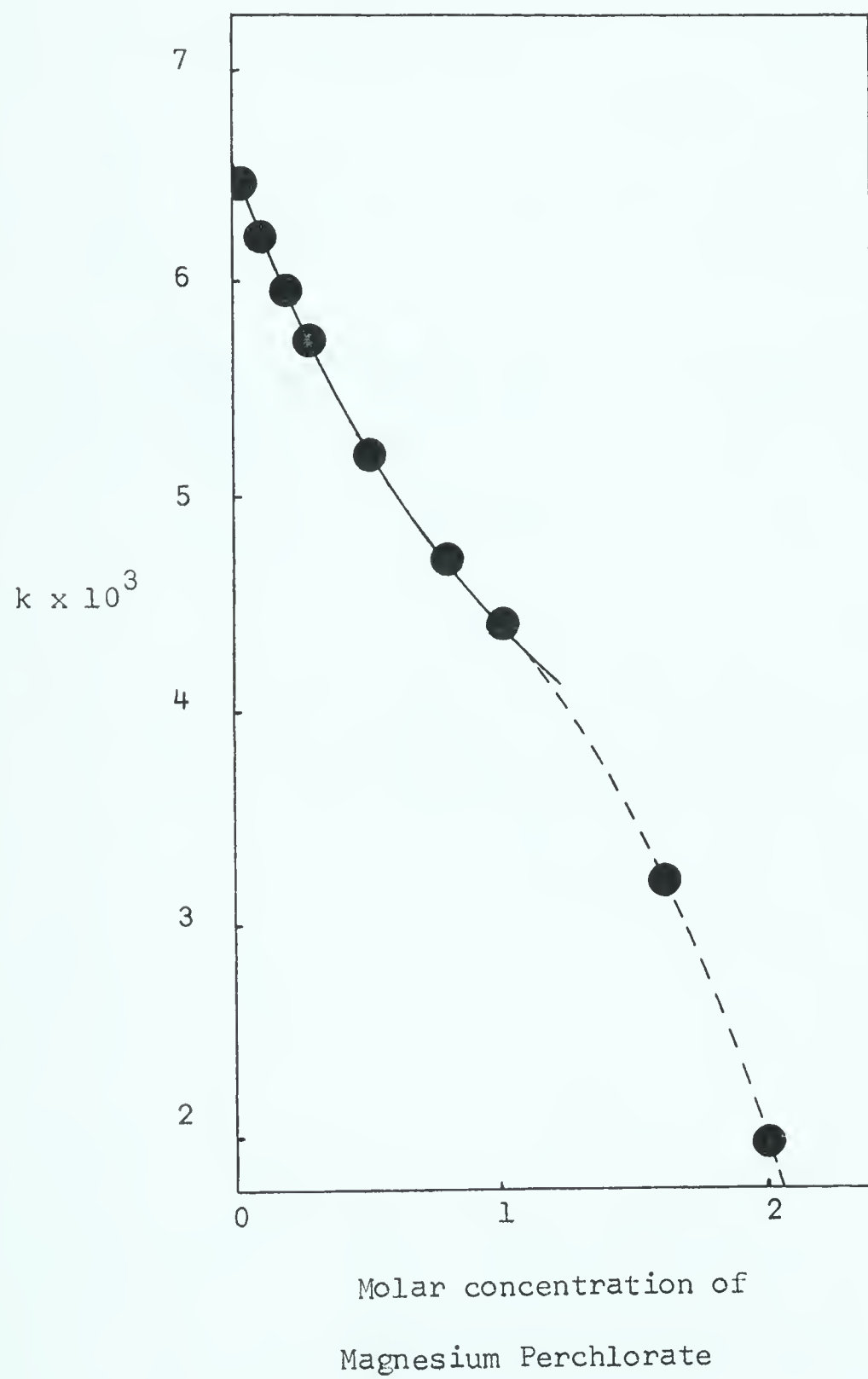
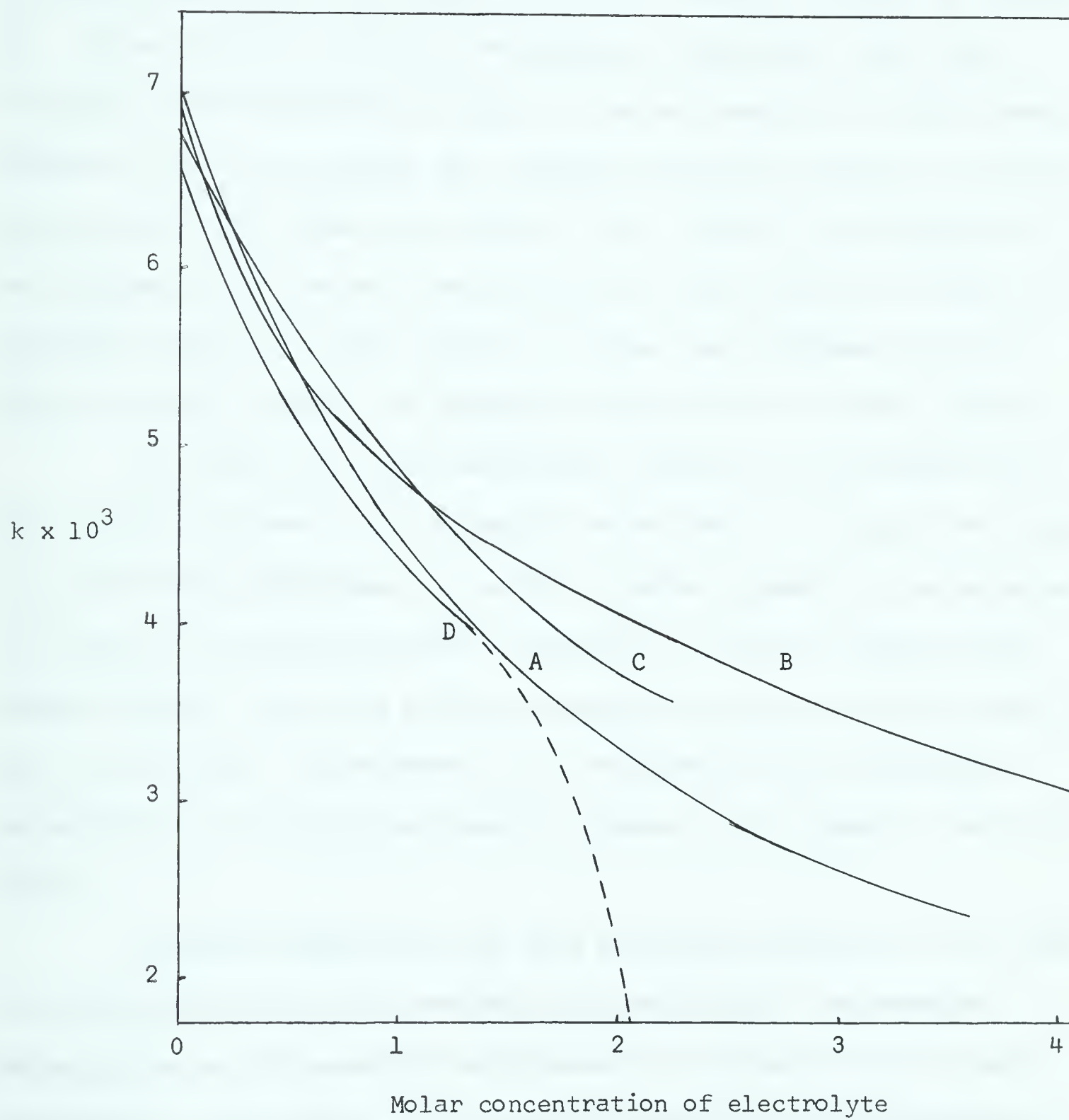


Figure 9

Comparison of the effect of perchlorate species on the
rate of aquation of bromopentamminechromium(III) cation
at 25.0°.

- A. Perchloric acid.
- B. Sodium perchlorate.
- C. Lithium perchlorate.
- D. Magnesium perchlorate.



Discussion

In studying the effect of pH on the aquation of bromopentammine-chromium(III) cation it had been observed (36), that the rate of aquation decreased with increasing hydrogen ion concentration below pH=1, while at pH values greater than 1 and less than 10 the reaction rate was pH independent. Since, at low pH, the ionic strength was necessarily larger than throughout the intermediate pH range, it was not possible to decide whether the decrease in the rate constant was a general electrolyte effect or a specific hydrogen ion effect. (See also section III-B) Specific participation of the hydrogen ion in the rate determining step should cause the effect of perchloric acid on the rate constant to appear quite different from the effect of sodium, lithium, or magnesium perchlorate on the rate constant.

For each of the four perchlorate electrolytes investigated the rate constant decreased with increasing concentration of electrolyte (figure 9). The concentration dependence of the rate constant appeared to be characteristic of the type of electrolyte present, especially at higher concentrations. However, figure 9 shows the effect of perchloric acid to be quite similar to that of its salts. The decrease in the rate constant with increasing concentrations of electrolyte therefore appears to be a general electrolyte effect.

Possible explanations for this electrolyte effect are to be based on an evaluation of how the reactants and possibly also the reaction mechanism can be influenced by the presence of a concentration of inert electrolyte. For instance, at low concentrations it is often possible to neglect activity coefficients, since either the coefficient itself or a ratio of coefficients usually approximates to unity (37). At high electrolyte concentrations activity coefficients seldom can be cancelled by such

approximations (38). Hence, if the solvent participates in the rate determining step, the effect of electrolyte concentration on its activity must also be taken into account. Bunnett (39), in considering the activity of water as a factor in reaction rates, has been able to classify acid catalyzed reactions at moderately high electrolyte concentrations from plots of $\log k$ vs. $\log /W/$. The dependence of the rate constant on the activity of water at higher concentrations is clearly shown.

Finally, since the increasing salt concentration lowers the dielectric constant, the possibility exists that a parallel mechanism involving ion - pairing may become increasingly important. This would mean that the cation or anion of the added electrolyte plays a role in the reaction intermediate. In order to minimize this possibility in the system under investigation monovalent and divalent perchlorate salts were chosen as the background electrolytes. Perchlorate ion would have a low (40) but constant tendency to ion - pair formation with the reactant, while the cations could associate only with the leaving group.

It was shown earlier (page 10) that the pseudo first order rate constant of the aquation reaction could be written as equation (XXII), where the value of n depends on the specific mechanism involved.

$$k = y_{MX} k_o / W^n \quad (XXII)$$

It was concluded that a plot of $\log(k/y_{MX}k_o)$ vs. $\log/W/$ should yield a straight line with slope equal to n . The main difficulty in constructing such a plot is that the values of y_{MX} are not even approximately known (see also section IV). However, if $\log y_{MX}$ remains reasonably constant over a range of electrolyte concentrations, a plot of $\log(k/k_o)$ vs. $\log/W/$ should, as a first approximation, yield a straight line with slope equal to n and

intercept $\log y_{MX}$ (from equation XXIII).

$$\log(k/k_o) = n \log/W/ + \log y_{MX} \quad (XXIII)$$

The activities of water over a range of concentrations for each of the perchlorate electrolytes were calculated from experimental osmotic coefficients (41) according to equation (XXIV), and are listed in table VIII.

$$\ln/W/ = -0.001 v m W \emptyset, \quad (XXIV)$$

where the symbols are defined as:

m - molality of electrolyte

v - the number of ions produced by a molecule of electrolyte

W - the molecular weight of the solvent

\emptyset - the molal osmotic coefficient.

These water activities and the rate data listed in tables IV, V, VI, and VII were used to plot $\log(k/k_o)$ vs. $\log/W/$ for each of the four electrolyte solutions used. The resultant plots are shown in figures (10), (11), (12), and (13). On each plot a dashed line is drawn which approximately shows the initial slope and which represents the apparent limiting value of n . Figure (14) shows the four individual plots together.

Over the range shown a smooth curve was obtained for each electrolyte. The initial slope varied from about 14 - 18 for the four electrolytes, while in each case the value of the slope decreased throughout the range plotted, with the values of the slopes at $-\log/W/ = .04$ ranging from about 3 - 7.

TABLE VIII

VALUES OF $-\log/W$ FOR VARIOUS SPECIES OF PERCHLORATE ELECTROLYTE,
CALCULATED FROM MOLAL OSMOTIC COEFFICIENTS"

<u>m</u>	<u>perchloric</u> <u>acid</u>	<u>lithium</u> <u>perchlorate</u>	<u>sodium</u> <u>perchlorate</u>	<u>magnesium</u> <u>perchlorate</u>
0.1	.0015	.0015	.0015	.0021
0.2	.0030	.0030	.0029	.0044
0.3	.0045	.0046	.0043	.0069
0.4	.0060	.0062	.0057	.0095
0.5	.0076	.0078	.0071	.0125
0.6	.0093	.0095	.0085	.0156
0.7	.0110	.0113	.0100	.0190
0.8	.0127	.0131	.0114	.0227
0.9	.0145	.0149	.0128	.0268
1.0	.0163	.0168	.0143	.0311
1.2	.0201	.0207	.0173	.0405
1.4	.0242	.0249	.0203	.0512
1.6	.0286	.0293	.0232	.0632
1.8	.0331	.0339	.0262	.0767
2.0	.0379	.0387	.0292	.0913

"molal osmotic coefficients obtained from (41).

Figure 10

PLOT OF $\log(k/k_0)$ vs. \log/W FOR PERCHLORIC ACID

The dashed line is the initial slope and represents
the maximum possible value of n . $n_{\max} = 18$.

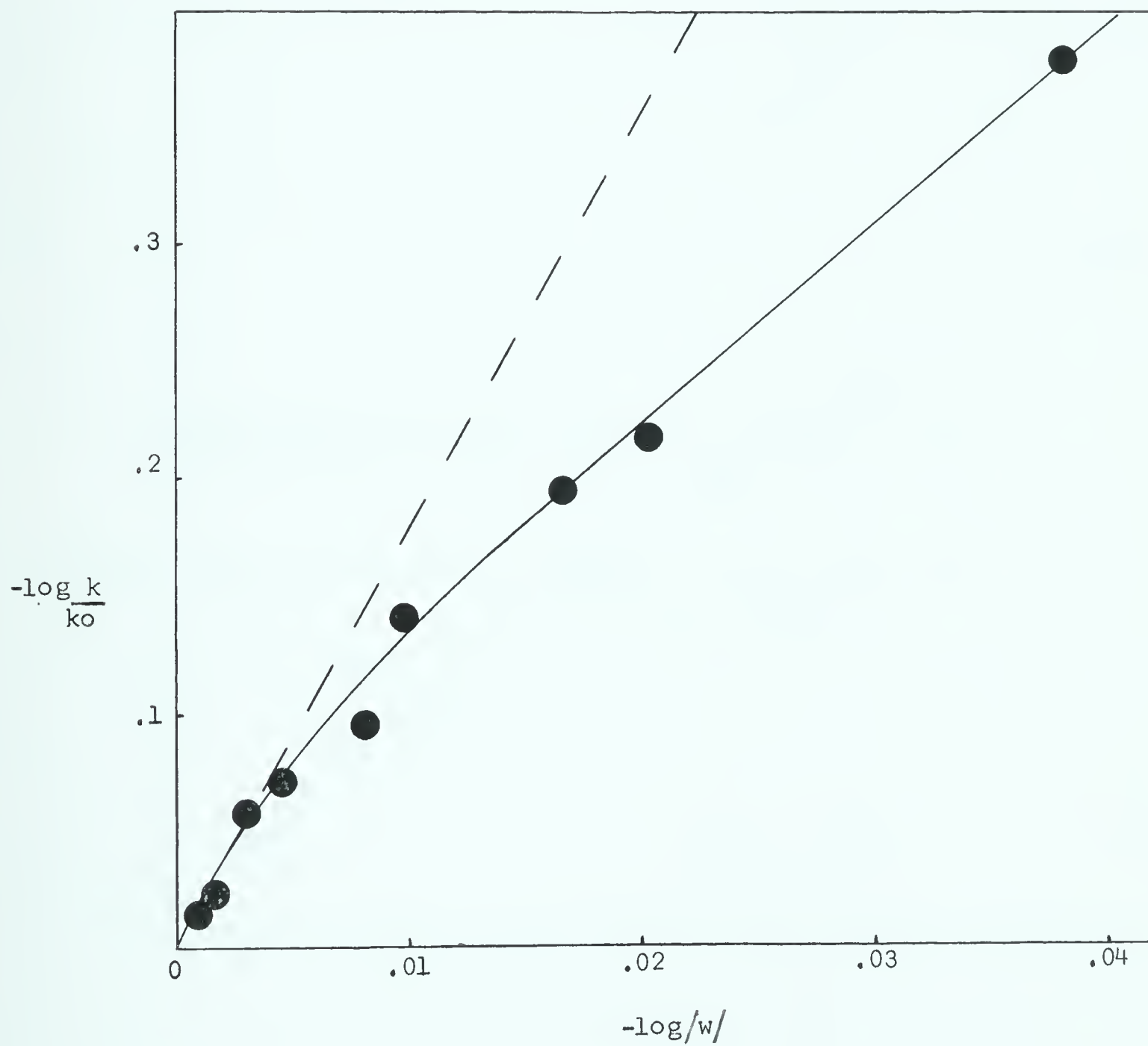


Figure 11

PLOT OF $\log(k/k_0)$ vs. $\log W$ FOR LITHIUM PERCHLORATE

The dashed line is the initial slope and represents
the maximum possible value of n . $n_{\max} = 14$.

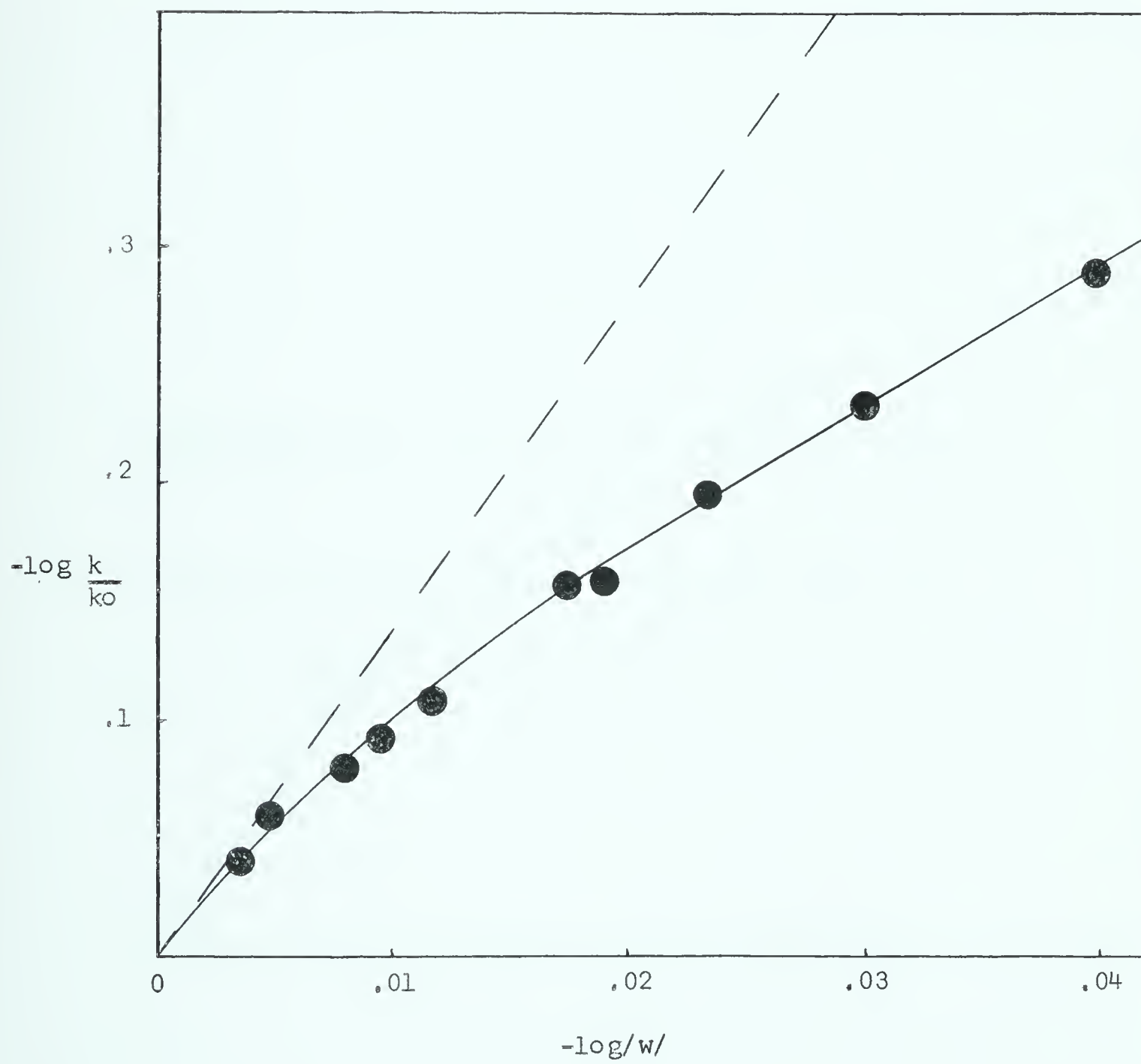


Figure 12

PLOT OF $\log(k/k_0)$ vs. $\log W$ FOR SODIUM PERCHLORATE

The dashed line is the initial slope and represents
the maximum possible value of n . $n_{\max} = 16$.

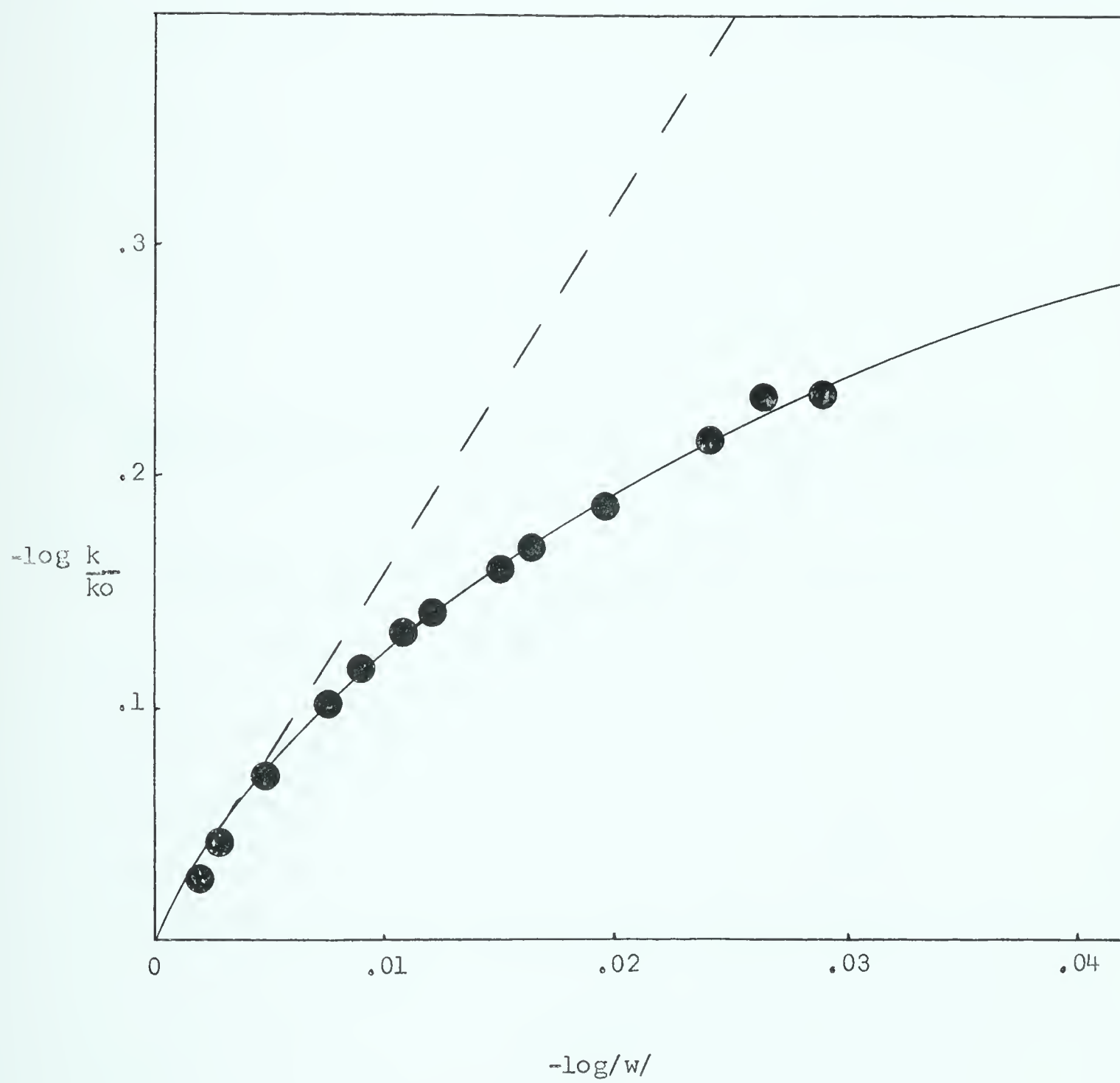


Figure 13

PLOT OF $\log(k/k_0)$ vs. $\log W$ FOR MAGNESIUM PERCHLORATE

The dashed line is the initial slope and represents
the maximum possible value of n . $n_{\max} = 14$.

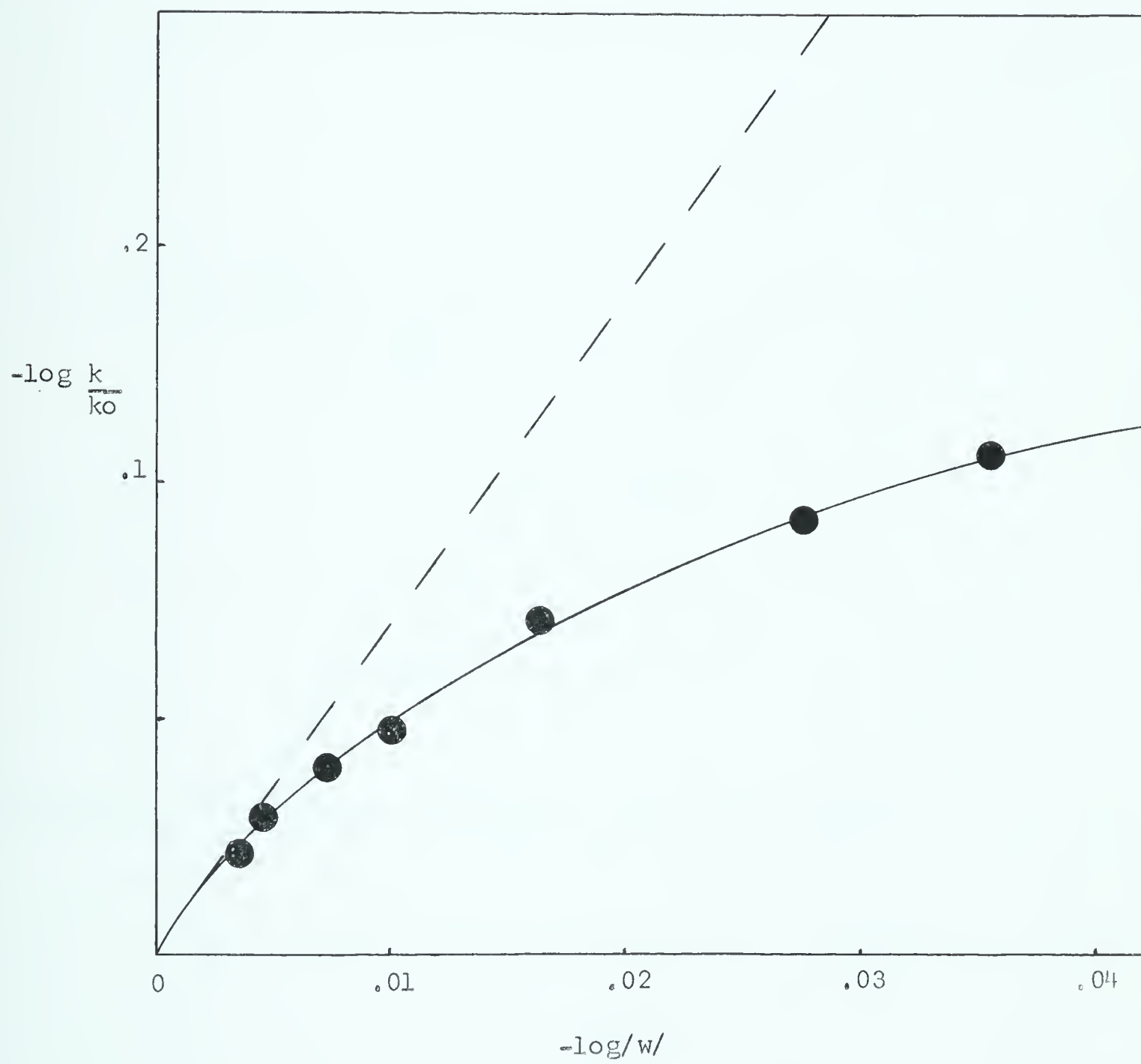


Figure 14

PLOT OF $\log(k/k_0)$ vs. $\log W$ USING THE COMBINED DATA OF

FIGURES 10, 11, 12, AND 13.

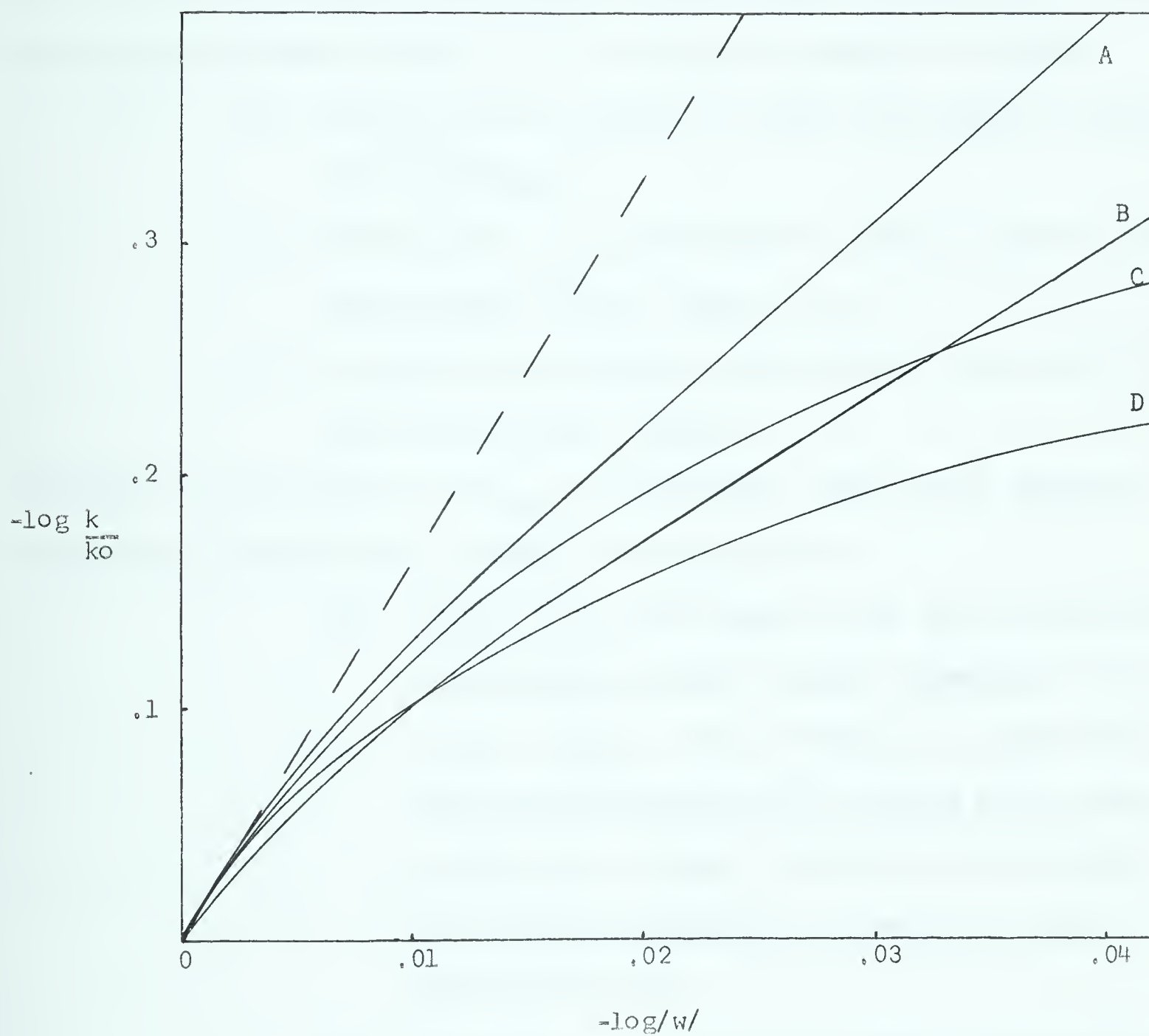
perchloric acid - A

lithium perchlorate - B

sodium perchlorate - C

magnesium perchlorate - D

The dashed line is the approximate initial slope and represents the maximum possible value of n . $n_{\max} = 17$.



Since both the activity of water and the rate constant decrease with increasing electrolyte concentration, some sort of correlation between them is to be expected. The physical picture presented by this model, which assumes $\log y_{MX}$ to be constant over a range of concentrations, can be correct only if there is a linear relationship between $\log W$ and $\log(k/k_0)$. In view of the results shown in figure 14 it is therefore apparent that either

- (a) $\log y_{MX}$ is not constant over any of the range of concentrations studied, or
- (b) other factors are responsible for both the curved plots and the high initial values of n , or
- (c) no physical relationship exists between the activity of water and the rate constant.

Although no exact values of $\log y_{MX}$ are available, some general statements concerning it can be made in support of statement (a):

- (1) values of y_{MX} will depend on the total concentration of electrolyte present and this dependence will probably be non - linear. From Section IV it appears that bromopentamminechromium(III) bromide can be expected to behave as a "normal" electrolyte and certainly the preceding statement is true for all such electrolytes (42).
- (2) values of y_{MX} at any but the lowest concentrations will depend upon the type of electrolyte present (43). This means that the neglect of $\log y_{MX}$ could be responsible for the non - linear as well as the individual nature of the four curves obtained, when $-\log(k/k_0)$ is plotted

against $-\log/W/$.

It is possible to get an idea of the variation of y_{MX} necessary to produce the observed curves (figure 14) by evaluating $[\log(k/k_o) - n \log/W/]$ for various values of n . Thus values of y_{MX} derived in this way are shown in tables IX, X, XI, and XII and plots of this function against concentration of electrolyte are given in figure 15. The plots are smooth curves, but individual points are not shown in an effort to avoid overcrowding the graphs. Although a quantitative comparison between the derived y_{MX} values and actual activity coefficient values is not possible, a qualitative appraisal can be made. It has been shown that, when a very small amount of one electrolyte is present along with a large excess of another electrolyte, the mean activity coefficient of the dilute species has a value intermediate to those of the separate electrolytes at the same total concentration (44). The mean activity coefficients of the perchlorate electrolytes have been reported (45). In Section IV an attempt is made to estimate the activity coefficient of the complex in the presence of a large excess of perchlorate electrolyte and to correlate these estimated values with values of y_{MX} derived above. The result of this attempt and its possible significance in terms of the kinetics of the aquation reaction are discussed in Section IV.

TABLE IX

VALUES OF y_{MX} IN PERCHLORIC ACID SOLUTIONS OF CONCENTRATION m FOR
 VARIOUS VALUES OF n

m	$n = 0$	$n = 5$	$n = 10$	$n = 15$
0.06	.972	.982	.992	1.002
0.1	.958	.975	.992	1.009
0.2	.875	.906	.937	.970
0.3	.847	.892	.940	.990
0.5	.806	.880	.961	1.049
0.6	.722	.804	.894	1.006
1.0	.639	.771	.930	1.121
1.2	.611	.770	.971	1.225
2.1	.431	.706	1.159	1.901

TABLE X

VALUES OF y_{MX} IN SODIUM PERCHLORATE SOLUTIONS OF CONCENTRATION m FORVARIOUS VALUES OF n

m	$n = 0$	$n = 5$	$n = 10$	$n = 15$
0.15	.945	.968	.993	1.018
0.2	.903	.933	.965	.997
0.35	.847	.895	.946	1.000
0.5	.792	.859	.933	1.013
0.6	.764	.843	.930	1.025
0.73	.736	.830	.935	1.054
0.8	.722	.823	.939	1.070
1.0	.694	.819	.965	1.137
1.1	.681	.816	.979	1.173
1.3	.654	.810	1.006	1.247
1.6	.611	.798	1.042	1.360
1.8	.583	.788	1.066	1.442
2.0	.583	.825	1.168	1.653

TABLE XI

VALUES OF γ_{MX} IN LITHIUM PERCHLORATE SOLUTIONS OF CONCENTRATION m FOR
VARIOUS VALUES OF n

m	$n = 0$	$n = 5$	$n = 10$	$n = 15$
0.2	.917	.947	.982	1.016
0.3	.875	.922	.972	1.024
0.5	.833	.912	.998	1.091
0.6	.806	.899	1.002	1.119
0.7	.778	.885	1.008	1.148
1.0	.694	.842	1.022	1.240
1.1	.694	.862	1.070	1.328
1.3	.639	.831	1.081	1.406
1.6	.583	.817	1.145	1.604
2.1	.514	.843	1.383	2.270

TABLE XII

VALUES OF y_{MX} IN MAGNESIUM PERCHLORATE SOLUTIONS OF CONCENTRATION m FOR

VARIOUS VALUES OF n

m	$n = 0$	$n = 5$	$n = 10$	$n = 15$
0.15	.903	.937	.973	1.010
0.2	.875	.920	.968	1.018
0.3	.833	.902	.976	1.056
0.4	.806	.899	1.003	1.120
0.6	.722	.864	1.034	1.238
0.9	.653	.888	1.209	1.644
1.1	.611	.915	1.370	2.050

Figure 15

PLOTS OF γ_{MX} VS. m FOR EACH ELECTROLYTE AT VARIOUS VALUES OF n .

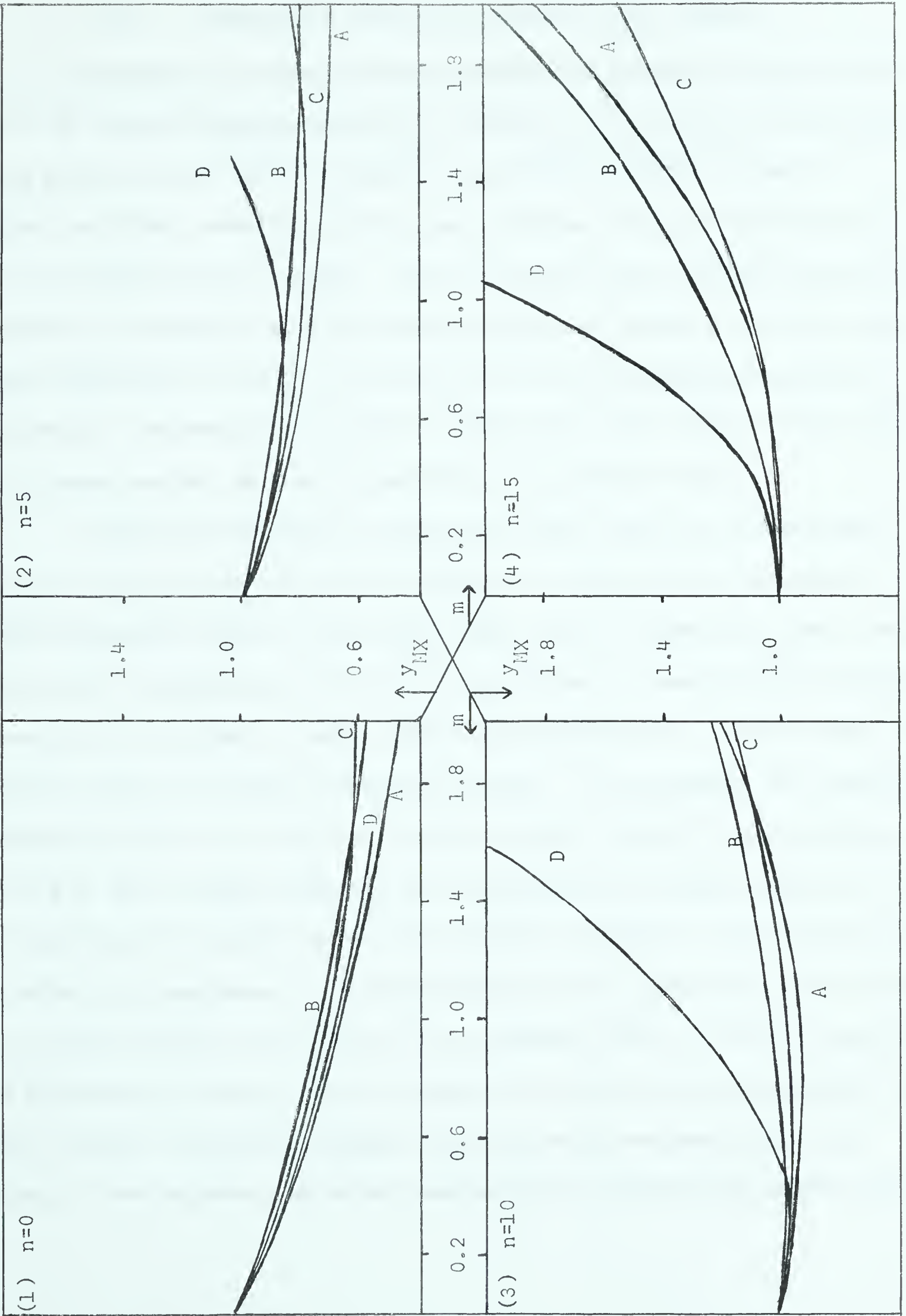
DATA FROM TABLES IX, X, XI, AND XII.

A - perchloric acid

B - lithium perchlorate

C - sodium perchlorate

D - magnesium perchlorate



III-B COMPOSITION EFFECTS AT CONSTANT IONIC STRENGTH

In order to be able to decide whether the decrease in the rate of aquation of bromopentamminechromium(III) bromide with increasing concentration of acid below $\text{pH}=1$ was due to a general electrolyte effect or a specific hydrogen ion effect, some kinetic data were obtained for portions of this pH region at constant ionic strength. The rate constant was measured with various proportions of perchloric acid and sodium perchlorate present, the total ionic strength being kept at 0.8 M, 2.0 M, and 4.4 M for three separate series of measurements. The results are listed in table XIV, while figure 17 shows the plots of rate constant against concentration of perchloric acid.

A specific hydrogen ion effect would show itself in a continuous decrease of the rate constant as the hydrogen ion concentration increased. A general electrolyte effect, on the other hand, would be expected to show the rate constant to be independent of the acid concentration at constant ionic strength. The results do not appear to agree with either possibility. Similar curves were obtained at each of the ionic strengths studied. As the hydrogen ion concentration increased from about 0.1 M the rate constant passed through a broad maximum at about 0.3 M, and at higher hydrogen ion concentration the peak levelled off into near linearity, the limiting slope being slightly negative. The explanation for this rather odd dependence of the rate constant on the composition of a constant ionic strength mixture can be found in the combined effect of the two electrolytes. It is significant, however, that the shape of the curve obtained presents strong evidence against a specific hydrogen ion effect being responsible for the decrease in rate constant, which had previously been observed below $\text{pH}=1$ (46).

TABLE XIV

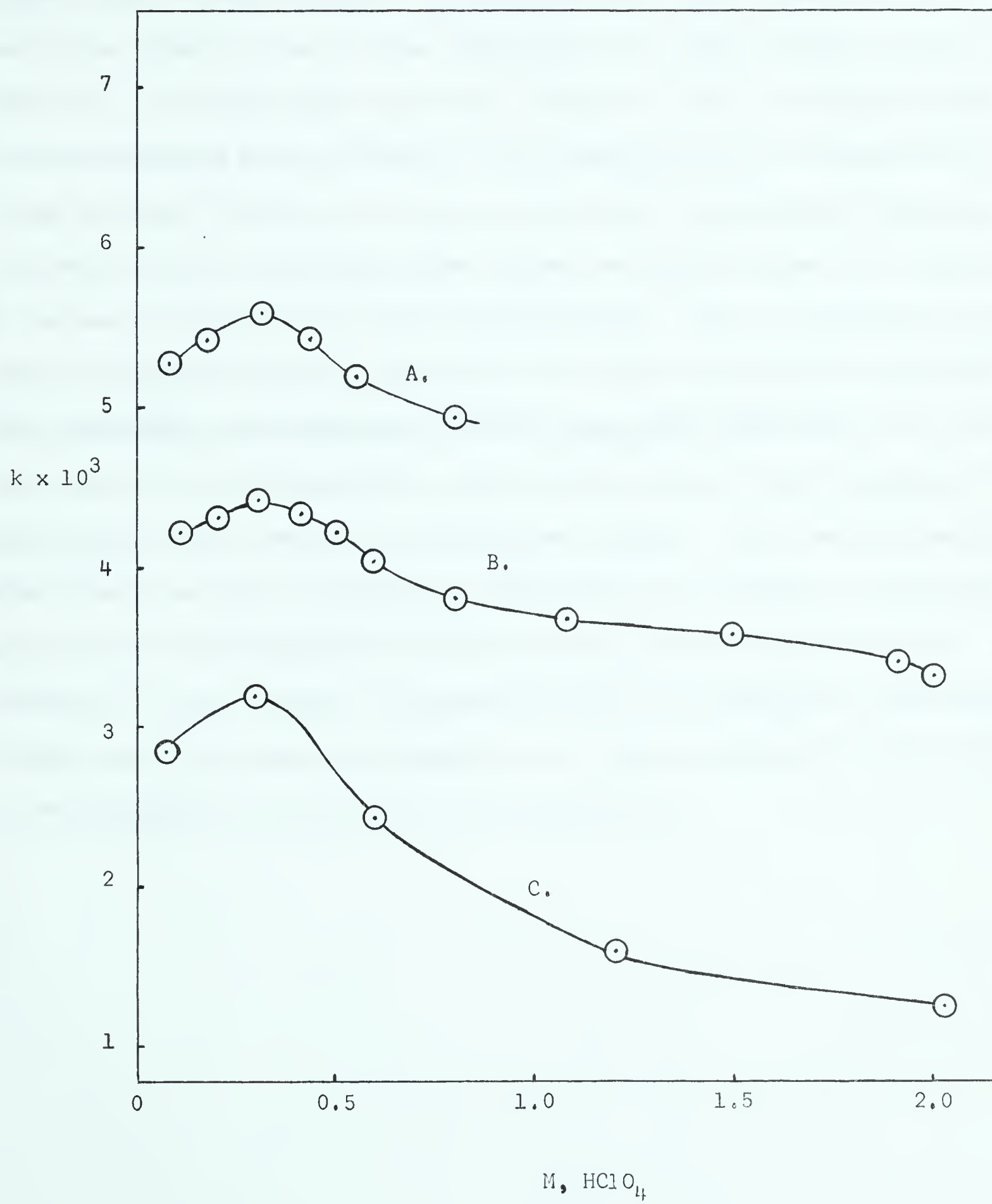
THE "HYDROGEN ION EFFECT" ON THE RATE CONSTANT AT CONSTANT IONIC STRENGTH

	<u>M. perchloric acid</u>	<u>M. sodium perchlorate</u>	<u>k x 10³</u>
A. u=0.8	0.06	0.74	5.2
	0.18	0.62	5.4
	0.31	0.49	5.6
	0.43	0.37	5.4
	0.55	0.25	5.2
	0.80	---	4.9
B. u=2.0	0.1	1.9	4.2
	0.2	1.8	4.3
	0.3	1.7	4.4
	0.4	1.6	4.3
	0.5	1.5	4.2
	0.6	1.4	4.0
	0.8	1.2	3.8
	1.1	0.9	3.7
	1.5	0.5	3.6
	1.9	0.1	3.4
	2.0	---	3.3
C. u=4.4	0.06	4.3	2.8
	0.3	4.1	3.2
	0.6	3.8	2.4
	1.2	3.2	1.6
	2.1	2.3	1.2

Figure 17

THE EFFECT OF HYDROGEN ION CONCENTRATION AT CONSTANT IONIC STRENGTH

- A. Ionic strength constant at 0.8 M.
- B. Ionic strength constant at 2.0 M.
- C. Ionic strength constant at 4.4 M.



Earlier it had been argued that a general electrolyte effect would show itself by the independence of the rate constant of the composition of the constant ionic strength mixture. This would be true only, however, if the electrolyte effects of each of the components of the ionic strength mixture were identical. It has been shown previously (figure 9), that the apparent effect of the perchlorates on the activity of the reacting species is characteristic of the particular "inert" salt at any but the lowest concentrations involved. This means that the electrolyte effect depends on species present (or composition in the case of a mixture) as well as concentration. This is illustrated to some extent in figures 18 and 19. At low perchloric acid concentrations the total effect approaches the characteristic sodium perchlorate effect and vice versa. The curvature at the intermediate concentrations indicates that the effect is not simply additive with respect to the component effects. Since the electrolyte effect itself is in all probability a combination of the effect of electrolyte concentration on such quantities as the activity of water and the activity coefficient of the reactant, the composite effect of a mixture on a combination of these quantities would not necessarily be a simple combination of the effects of the components of the mixture on these quantities.

Figure 18

CONSTANT IONIC STRENGTH EFFECT IN TERMS OF COMPONENTS EFFECTS

- A. Perchloric acid only
- B. Sodium perchlorate only
- C. Perchloric acid and sodium perchlorate at
constant ionic strength of 2.0 M.

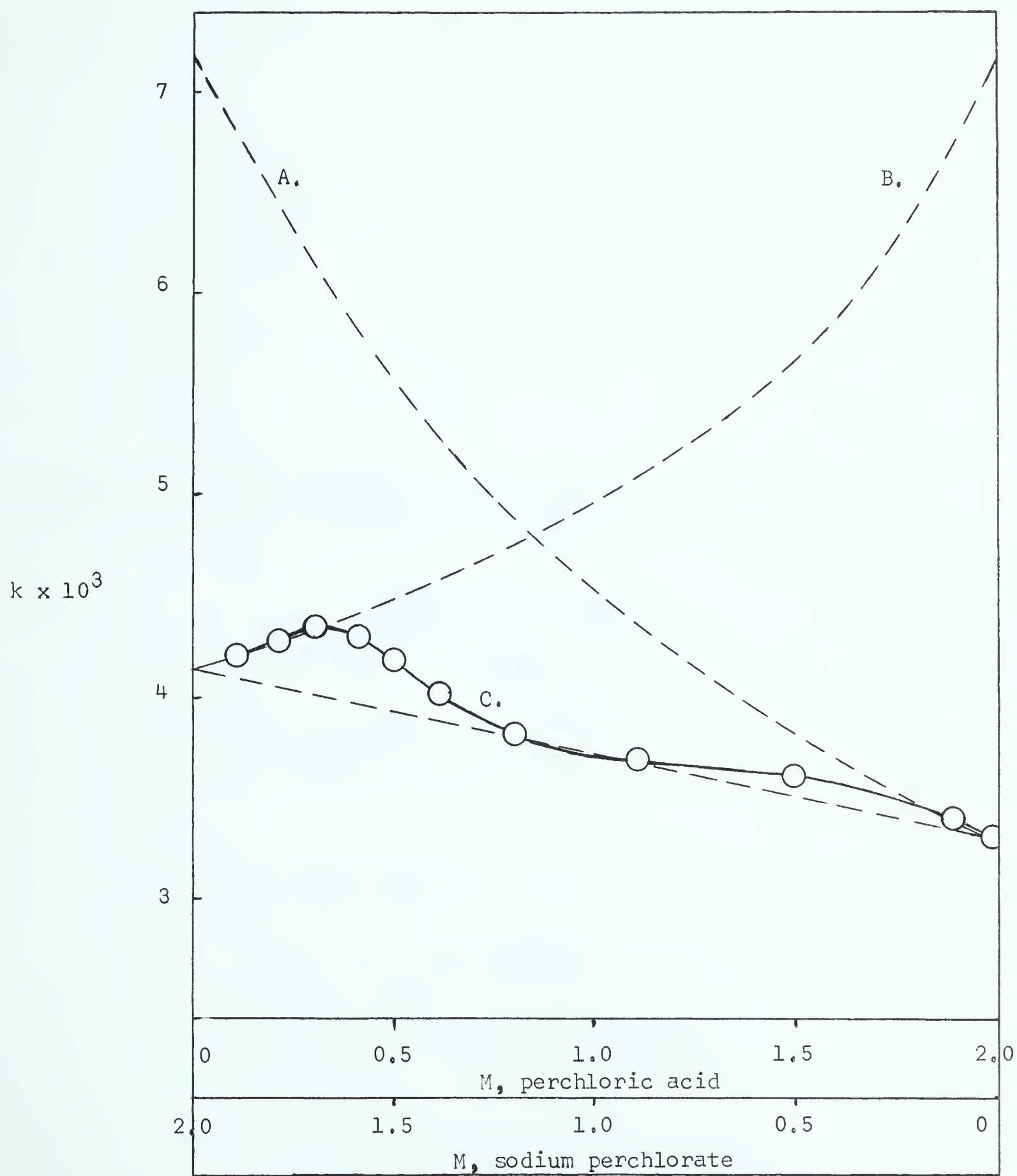
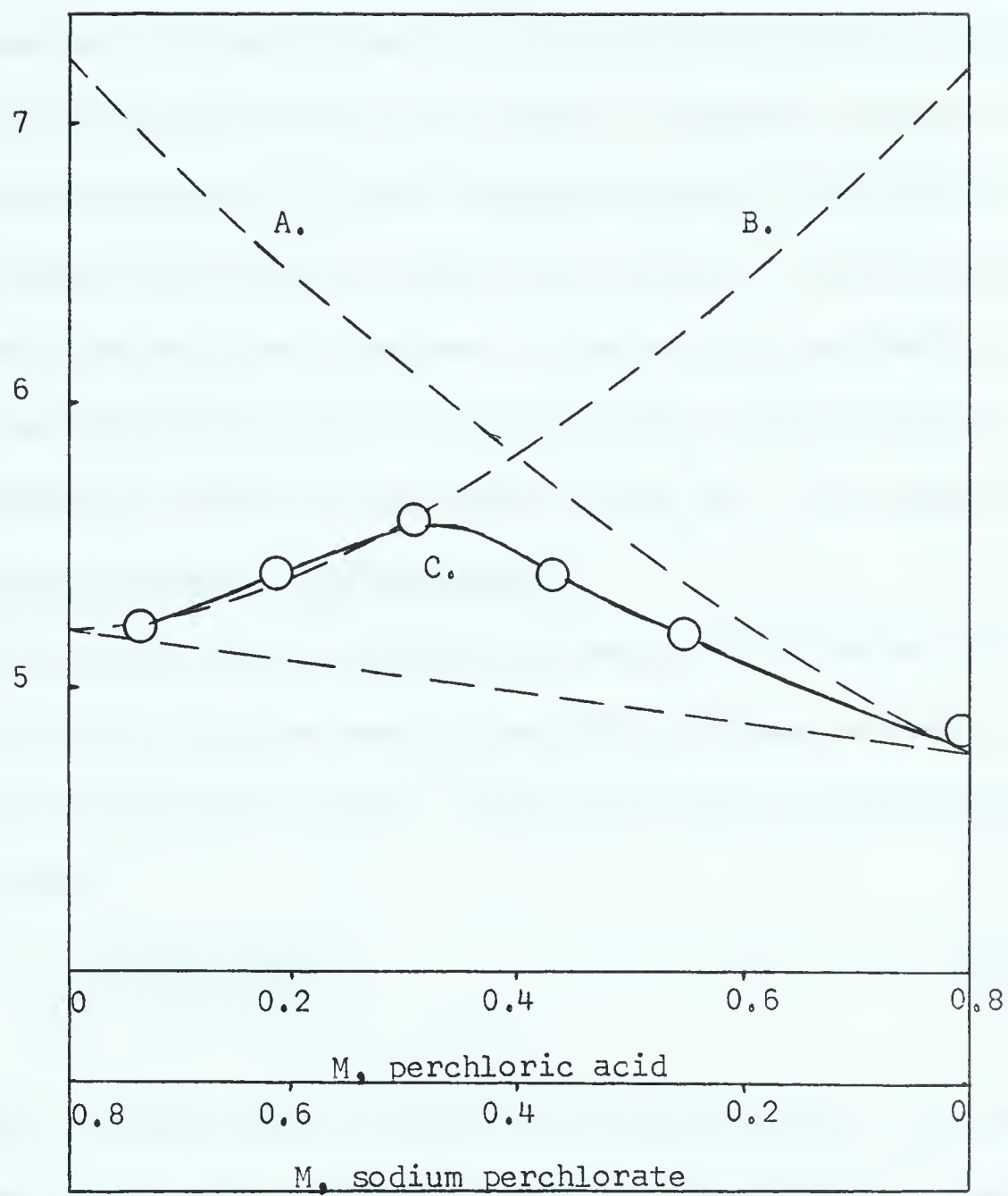


Figure 19

CONSTANT IONIC STRENGTH EFFECT IN TERMS OF COMPONENTS EFFECTS

- A. Perchloric acid only
- B. Sodium perchlorate only
- C. Perchloric acid and sodium perchlorate
at constant ionic strength of 0.8 M.



IV EVALUATION OF THE ACTIVITY COEFFICIENT

In order to be able to explain the effect of high concentrations of electrolyte on the rate of aquation of the bromopentamminechromium(III) cation it is necessary to know the effect of high concentrations of electrolyte on the activity coefficient of the complex ion, as shown in equation XXIII. However, the behaviour of electrolytes in concentrated solutions cannot at present be quantitatively described by any strict theoretical method (47). The behaviour of electrolytes in dilute solutions has been described in terms of meaningful concepts and parameters and can be used as a starting point in explaining concentrated solution behaviour. However, such extensions of the theory of dilute solutions are usually of an empirical nature because of lack of quantitative understanding of short range ion - ion interactions (48).

The Rearranged Extended Debye - Huckel Equation

For dilute solutions of a single electrolyte the Extended Debye - Huckel Equation (E.D.H.E.) can be used to calculate the mean activity coefficient of many electrolytes (49). The equation for an aqueous solution at 25° is given by (XXV),

$$-\log y = \frac{0.5083 \, ZZ' \sqrt{u}}{1 + 0.3282 \, a \sqrt{u}} \quad (\text{XXV})$$

where y represents the mean molal activity coefficient, Z and Z' the absolute charge on the cation and anion of the electrolyte respectively, u the ionic strength, and a the distance of closest approach between cation and anion in solution. More sophisticated and at the same time more empirical forms of the equation have additional terms added to the right hand side of equation (XXV) (50). The addition of a term linear in concentration extends the range of concentrations over which the equation can be used considerably (51). Robinson

and Stokes (52) have taken into account the influence of ion - solvent interactions on the activity coefficient, the result being the two parameter equation given by (XXVI),

$$-\log y = \frac{A ZZ' \sqrt{u}}{1 + \frac{B}{a} \sqrt{u}} + \frac{h}{v} \log a_A + \log [1 + 0.001 W_A (v - h)m] \quad (\text{XXVI})$$

where A and B are the constants of the E.D.H.E., h is the hydration number of one solvated electrolyte molecule, v is the number of ions per molecule, a_A is the activity of the solvent, W_A is the molecular weight of the solvent, and m is the molality. For non - associated 1 : 1 and 2 : 1 electrolytes equation (XXVI) has been found valid up to moderately high concentrations, the limit of validity generally being reached when $hm \approx 12$, i.e. when about one quarter to one fifth of the solvent is involved in solvation of the electrolyte ions (53).

While additional terms such as those described above do extend the range of use of the E.D.H.E., they are of a more or less empirical nature and require for their practical use the knowledge of one or more additional empirical constants. For the purpose of this treatment a term Y is defined as the correction term necessary to make the E.D.H.E. conform to experimental results, as shown by equation (XXVII). This is not serious since the following treatment of the

$$-\log y = \frac{0.5083 ZZ' \sqrt{u}}{1 + 0.3282 \frac{\sqrt{u}}{a}} + Y \quad (\text{XXVII})$$

equation is independent of the form or complexity of Y.

The E.D.H.E. as given above (equation XXVII) predicts a curved relationship between $-\log y$ and \sqrt{u} , and, as a consequence, graphical treatment and comparison of data are difficult. Rearrangement of equation (XXVII) produces a relationship (equation XXVIII) which is linear at sufficiently low concentrations.

$$-\frac{1}{\log y} = \left(\frac{1}{\sqrt{u}}\right)\left(\frac{1.967}{ZZ'}\right)\left(1 + \frac{Y}{\log y}\right) + \frac{o}{a}\left(\frac{0.6457}{ZZ'}\right)\left(1 + \frac{Y}{\log y}\right) \tag{XXVIII}$$

Equation (XXVIII) is obtained by multiplying equation (XXVII) through by the denominator of the first term on the right hand side of equation (XXVII), dividing through by $(-\log y) \times u$, and collecting the appropriate terms. Equation (XXVIII) states that for $Y=0$, i.e. at sufficiently low concentrations, a linear relationship exists between $-1/\log y$ and $1/\sqrt{u}$, and a plot of $-1/\log y$ vs. $1/\sqrt{u}$ should give a straight line with a slope which is dependent only on the charges of the ions, and an intercept which is dependent on the value of $\frac{o}{a}$ as well as the charges on the ions. The ionic strength, u , is given in terms of concentration by $u = 1/2\sum_i c_i Z_i^2$, which for each charge type of electrolyte simplifies to $u=nc$, where n is a constant dependent on the charge type of electrolyte. Values of n for various types of electrolytes are given in table XV. Equation (XXVIII) can therefore be written in terms of concentration (equation XXIX), and, for $Y=0$, a plot of $-1/\log y$ vs. $1/\sqrt{c}$ should also give a straight line, with a slope which is dependent on the charge type of the electrolyte. Values of the theoretical slopes of such

$$-\frac{1}{\log y} = \frac{1}{\sqrt{c}}\left(\frac{1.967}{ZZ'\sqrt{n}}\right)\left(1 + \frac{Y}{\log y}\right) + \frac{o}{a}\left(\frac{0.6457}{ZZ'}\right)\left(1 + \frac{Y}{\log y}\right) \tag{XXIX}$$

plots are given for various types of electrolytes in table XV.

TABLE XV

VALUES OF n AND OF THE THEORETICAL SLOPES FROM EQUATION XXIX FOR VARIOUS TYPES OF ELECTROLYTES		
Type of Electrolyte	Value of n in $u=nc$	Theoretical slope = $\frac{1.967}{ZZ'\sqrt{n}}$
1 : 1	1	1.97
2 : 1	3	0.57
3 : 1	6	0.27
2 : 2	4	0.25
3 : 2	15	0.08

The condition $Y=0$ corresponds to that region of concentration where E.D.H.E. (equation XXV) applies. A linear relationship between $-1/\log y$ and $1/\sqrt{c}$ does not necessarily mean, however, that the E.D.H.E. is valid over the range of linearity. The E.D.H.E. is valid only in those cases where the plot is linear and the value of the slope agrees with the theoretical value given in table XV.

The activity coefficients for a number of compounds have been reported at concentrations as low as 0.001 M (54), and for these data plots were constructed of $-1/\log y$ vs. $1/\sqrt{c}$. Additionally, values of \bar{a}° were calculated from these data by solving equation (XXV) for \bar{a}° at each concentration of electrolyte for which an activity coefficient was reported. The detailed results for potassium chloride, calcium chloride, and lanthanum chloride are given in tables XVI, XVII, and XVIII, and figures 20, 21, and 22. The plots are linear over a considerable range of concentrations; the concentration at which the plot first deviates from a straight line is about 1.4 M for potassium chloride, 0.2 M for calcium chloride, and 0.05 M for lanthanum chloride. The slopes of the straight line portions are 1.97, 0.57, and 0.27 respectively, and the values of \bar{a}° obtained from the intercept are 4.0, 5.3, and 5.6 Å respectively. The calculated values of \bar{a}° are also consistent over a range of concentrations; for potassium chloride $\bar{a}^\circ = 4.0 \pm 0.1$ from 0.005 to 1.4 M, for calcium chloride $\bar{a}^\circ = 5.2_5 \pm 0.1$ from 0.002 to 0.1 M, and for lanthanum chloride $\bar{a}^\circ = 6.0 \pm 0.1$ from 0.001 to 0.02 M. The results obtained for potassium chloride, calcium chloride, and lanthanum chloride represent cases of favourable agreement with the E.D.H.E. for three types of electrolytes.

The results for a number of compounds are summarized in tables XIX, XX, and XI. Values of \bar{a}° reported by two independent sources (55, 56)

TABLE XVI

VALUES OF $-1/\log y$ AND $1/\sqrt{C}$ FOR POTASSIUM CHLORIDE, OBTAINED FROM
PUBLISHED MEAN MOLAL ACTIVITY COEFFICIENTS (54).

<u>Molality, C</u>	<u>Activity coeff. y (54).</u>	<u>$1/\sqrt{C}$</u>	<u>$-1/\log y$</u>	<u>$\log a$ calculated from E.D.H.E.</u>
0.001	.965	31.64	64.52	3.53
0.002	.952	22.37	46.73	4.23
0.005	.927	14.14	30.40	4.00
0.01	.902	10.00	22.32	4.10
0.02	.869	7.07	16.39	3.84
0.05	.816	4.47	11.33	3.92
0.1	.770	3.16	8.81	4.01
0.2	.718	2.24	6.95	3.95
0.3	.688	1.83	6.16	3.98
0.4	.666	1.58	5.67	3.97
0.5	.649	1.41	5.32	3.93
0.6	.637	1.29	5.10	3.97
0.7	.626	1.19	4.92	3.98
0.8	.618	1.12	4.78	4.00
0.9	.610	1.05	4.66	4.01
1.0	.604	1.00	4.57	4.03
1.2	.593	0.92	4.41	4.04
1.4	.586	0.84	4.31	4.10
1.6	.580	0.79	4.23	4.15
1.8	.576	0.75	4.17	4.18
2.0	.573	0.71	4.14	4.26
2.5	.569	0.63	4.08	4.40
3.0	.569	0.58	4.08	4.55

TABLE XVII

VALUES OF $-1/\log y$ AND $1/\sqrt{C}$ FOR CALCIUM CHLORIDE, OBTAINED FROM
PUBLISHED MEAN MOLAL ACTIVITY COEFFICIENTS (54).

<u>Molality C</u>	<u>Activity coeff. y (54)</u>	<u>$1/\sqrt{C}$</u>	<u>$-1/\log y$</u>	<u>α calculated from E.D.H.E.</u>
0.001	.889	31.64	19.57	4.96
0.002	.852	22.37	14.37	5.17
0.005	.789	14.14	9.72	5.23
0.01	.731	10.00	7.35	5.17
0.02	.668	7.07	5.71	5.23
0.05	.583	4.47	4.27	5.36
0.1	.518	3.16	3.50	5.30
0.2	.472	2.24	3.07	5.57
0.3	.455	1.83	2.92	5.82
0.4	.448	1.58	2.87	6.10
0.5	.448	1.41	2.87	6.38

TABLE XVIII

VALUES OF $-1/\log y$ AND $1/\sqrt{C}$ FOR LANTHANUM CHLORIDE, OBTAINED FROM
PUBLISHED MEAN MOLAL ACTIVITY COEFFICIENTS (54).

<u>C</u>	<u>y (54)</u>	<u>$1/\sqrt{C}$</u>	<u>$-1/\log y$</u>	<u>$\frac{o}{a}$</u>
0.001	.790	31.64	9.77	6.04
0.002	.729	22.37	7.28	5.99
0.005	.636	14.14	5.09	6.04
0.01	.560	10.00	3.97	5.99
0.02	.483	7.07	3.16	5.90
0.05	.388	4.47	2.43	3.81
0.1	.314	3.16	1.99	5.30
0.2	.274	2.24	1.78	5.48
0.3	.263	1.83	1.72	5.72

Figure 20

Plot of $-1/\log y$ vs. $1/\sqrt{C}$ for potassium chloride.

Data from (54).

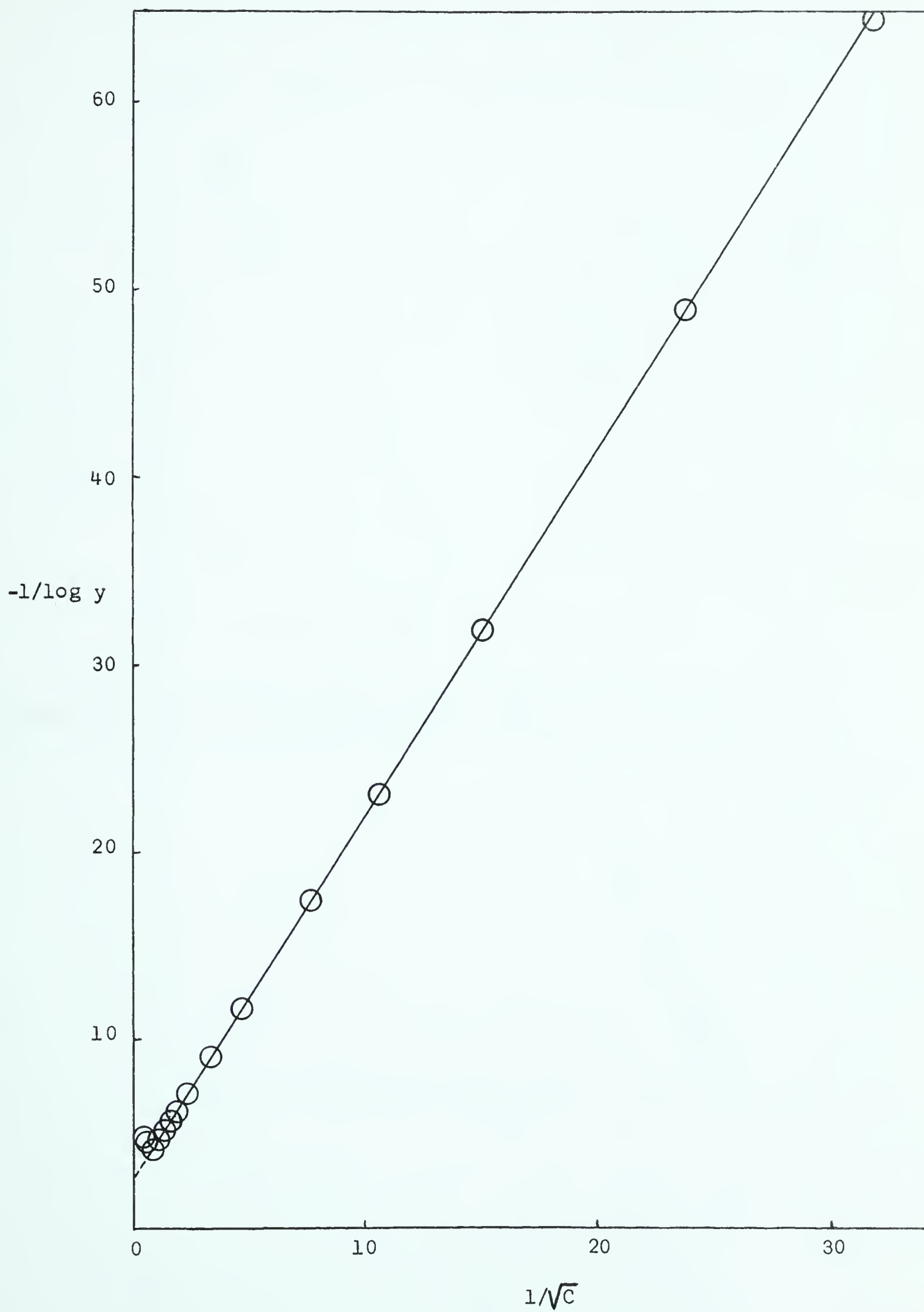


Figure 21

Plot of $-1/\log y$ vs. $1/\sqrt{c}$ for calcium chloride. Data from (54).

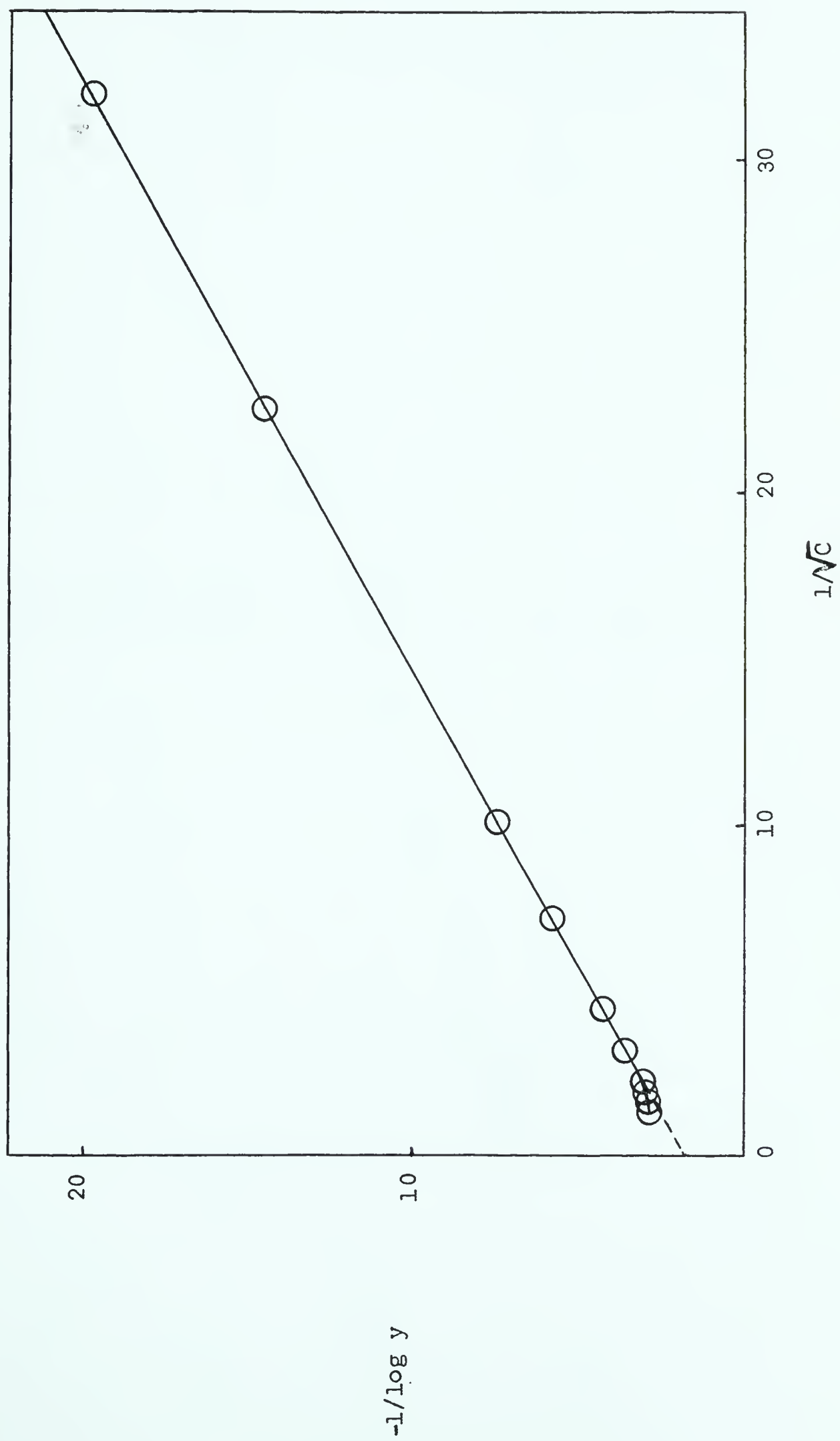


Figure 22

Plot of $-1/\log y$ vs. $1/\sqrt{c}$ for lanthanum chloride. Data from (54).

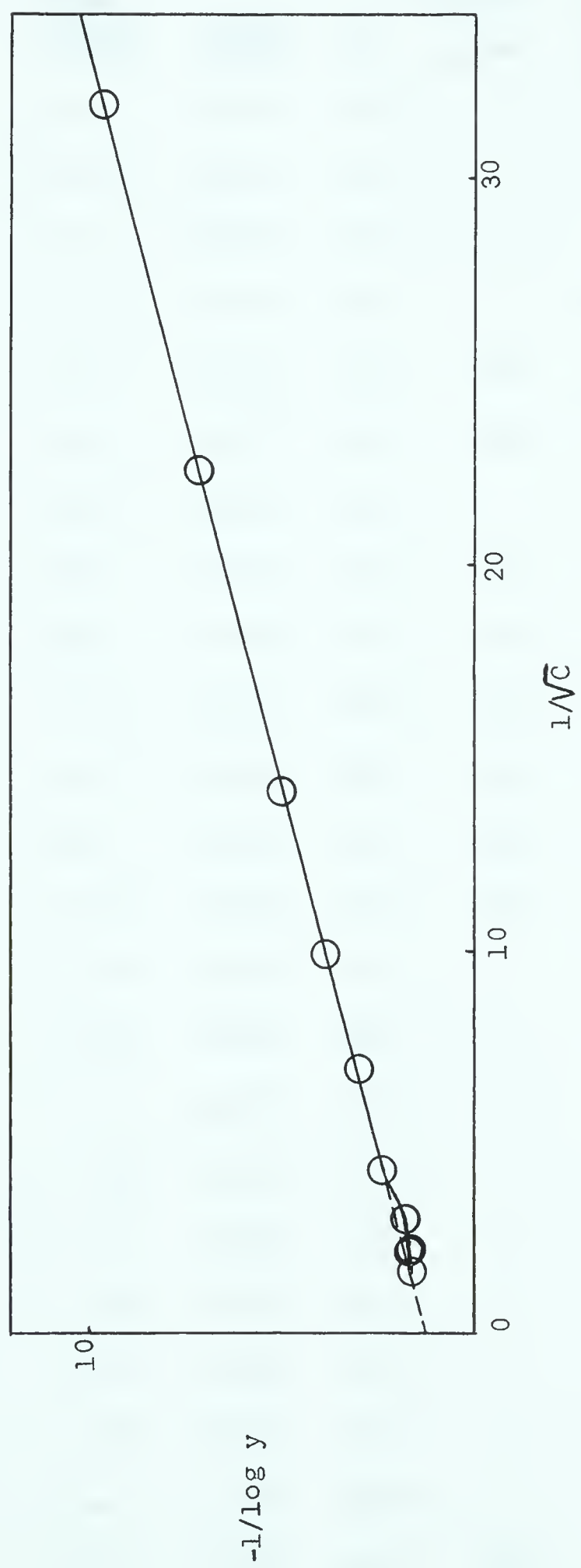


TABLE XIX
COMPARISON OF $\frac{o}{a}$ VALUES OBTAINED FROM VARIOUS SOURCES FOR 1:1 ELECTROLYTES

<u>Electrolyte</u>	<u>G R A P H I C A L L Y</u>		<u>C A L C U L A T E D</u>				Associ- ation constant (57, 58)
	Conc. range fitted	slope	$\frac{o}{a}$	$\frac{E.D.H.E.}{a}$	Ref. (55) $\frac{o}{a}$	Ref. (56) $\frac{o}{a}$	
Hydrochloric acid	- .01	1.95	5.0		4.5	4.3	
Hydrobromic acid	- .02	1.98	5.8		5.2	4.4	
Hydrofluoric acid	- .1	0.09	1.0				1500
Lithium chloride	- .05	1.70	6.0		4.3	4.3	
Lithium bromide	- .2	1.97	7.0	6.9	4.6	4.3	
Sodium chloride	- .4	1.97	4.6	4.5	4.0	4.2	0.1
Sodium bromide	- .4	1.89	5.2		4.2	4.2	
Potassium chloride	-1.0	1.97	4.0	4.0	3.6	3.9	
Potassium bromide	-1.0	1.96	4.3	4.2	3.9	3.9	0.4
Potassium iodide	- .3	1.97	4.5	4.6	4.2	4.0	
Rubidium chloride	-1.0	1.99	3.6	3.5	3.5	3.2	0.16
Cesium chloride	-1.0	2.02	2.8	2.8		2.5	0.4
Ammonium chloride	- .02	1.98	1.9	4.0	3.8		
Sodium chlorate	- .05	1.96	4.8				
Sodium bromate	- .02	2.22	3.6				0.3
Sodium iodate	- .1	2.02	0.8				0.3
Potassium chlorate	- .02	2.18	2.7				0.9
Potassium perchlorate	- .2	2.03	0.7				0.3
Nitric acid	- .05	1.92	4.9				0.04
Lithium nitrate	- .3	1.98	5.9				4.4
Sodium nitrate	- .05	2.01	4.4				0.3
Potassium nitrate	- .4	2.00	2.3				0.6
Ammonium nitrate	- .1	1.97	2.2	2.2			

TABLE XX
COMPARISON OF \bar{a} VALUES FROM VARIOUS SOURCES FOR MULTIVALENT ELECTROLYTES

<u>Electrolyte</u>	<u>G R A P H I C A L L Y</u>			<u>C A L C U L A T E D</u>			Associ- ation constant (57, '58)
	Conc. range fitted	slope	\bar{a}	E.D.H.E. \bar{a}	Ref. (55) \bar{a}	Ref. (56) \bar{a}	
Calcium chloride	- .5	0.57	5.3	5.2	4.7		
Strontium chloride	- .2	0.62	6.9		4.6		
Barium chloride	- .5	0.52	5.6		4.5		
Cupric chloride	- .3	0.57	4.5	4.3			1.1
Zinc chloride	- .05	0.52	4.6				1.5
Zinc iodide	- .1	0.55	7.2	6.8			20
Cadmium chloride	-1.0	0.31	1.7				100
Cadmium bromide	-1.0	0.25	1.8				150
Cadmium iodide	-1.0	0.19	1.3				250
Barium nitrate	- .02	0.54	3.7				9
Magnesium nitrate	- .05	0.52	5.1				
Barium hydroxide	- .2	0.57	3.4	3.2			4.4
Selenic acid	- .1	0.22	3.1				110
Sulfuric acid	-1.0	0.30	2.5				97
Sodium sulphate	- .1	0.57	3.4				5
Potassium sulphate	- .02	0.57	3.3				9
Calcium thiosulphate	- .005	0.25	1.2				90
Cadmium sulphate	- .05	0.22	2.3	2.9			230
Zinc sulphate	- .005	0.19	2.2	3.0			210
Cupric sulphate	- .05	0.24	1.8	3.0			230
Cerium(III) chloride	- .4	0.27	5.6	5.7			0.8
Lanthanum chloride	- .4	0.27	5.6	6.0			0.8
Indium sulphate	- .4	0.07	3.9	3.9			100

TABLE XXI

RESULTS FROM PLOTS OF $-1/\log y$ VS. $1/\sqrt{c}$ FOR SOME COBALT(III) AND
CHROMIUM(III) COORDINATION COMPOUNDS

Letter code	Compound	Conc. range fitted(c)	slope	$\frac{o}{a}$	$\frac{o}{a}$ from ref.	Refer- ence to data
A	$[\text{Co(en)}_3]\text{Cl}_3$	- .35	0.28	3.0	3.4	(59)
B	$[\text{Co(en)}_3](\text{ClO}_4)_3$	- .07	0.27	4.0	4.0"	(60)
C	$[\text{Co(en)}_3](\text{NO}_3)_3$	- .1	0.27	3.3	3.2	(61)
D	$[\text{Co(pn)}_3](\text{ClO}_4)_3$	- .15	0.28	3.1	3.2	(61)
E	$[\text{Co(en)}_3](\text{SO}_4)_3$	- .2	0.08 ₅	3.4	3.4	(61)
F	$[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$	-----	-----	5.3"	-----	(62)
G	$[\text{Cr}(\text{H}_2\text{O})_6](\text{NO}_3)_3$	-----	-----	5.3"	-----	(62)
H	$[\text{Cr}(\text{H}_2\text{O})_6]_2(\text{SO}_4)_3$	- .6	0.09 ₅	4.1	-----	(62)

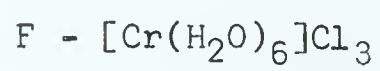
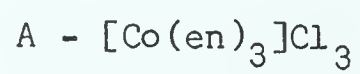
en - ethylenediamine

pn - propylenediamine

" - estimated

Figure 23

PLOTS OF $-1/\log y$ VS. $1/\sqrt{m}$



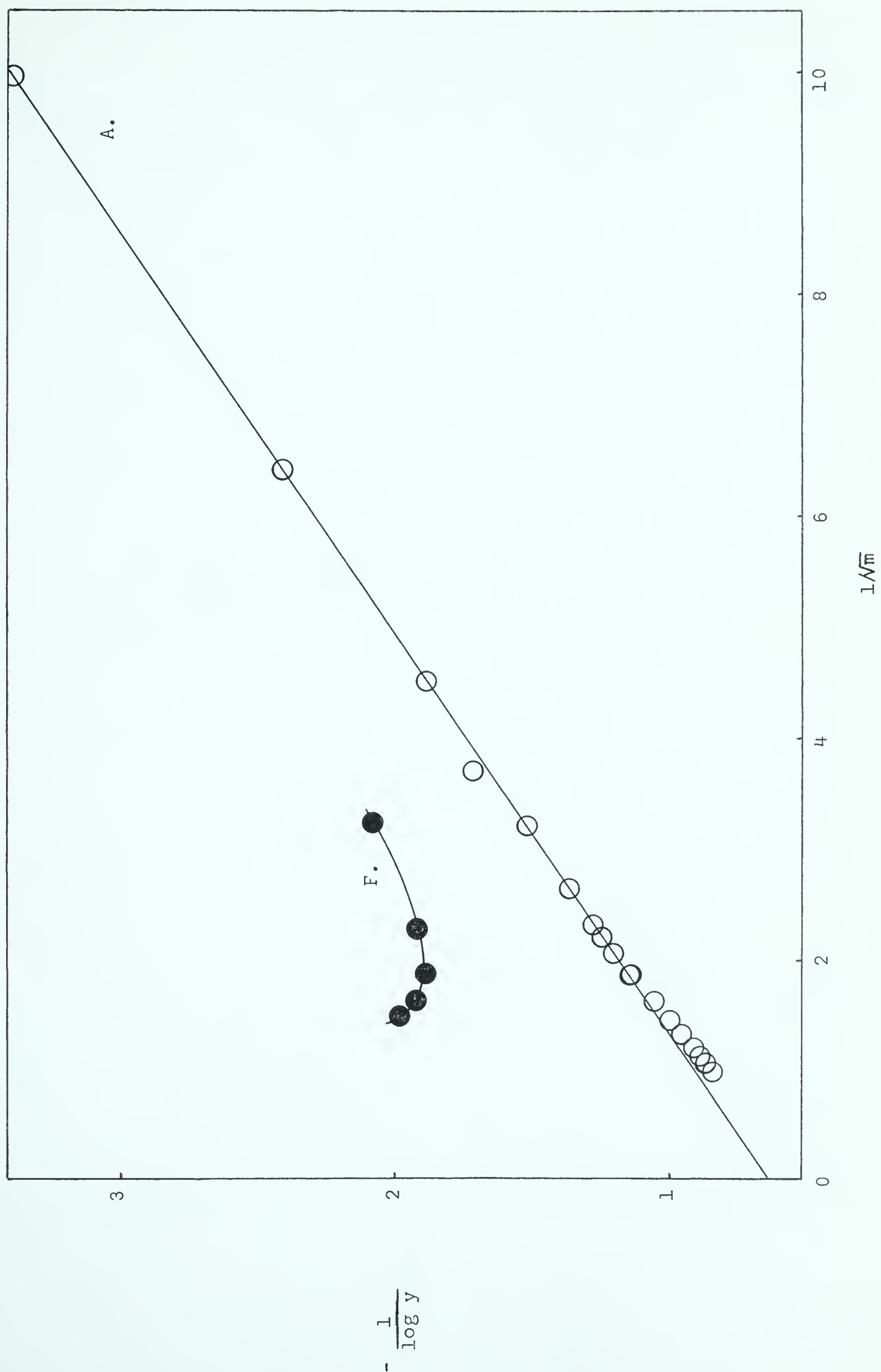
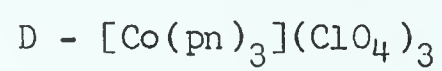
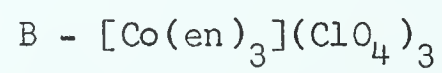


Figure 24

PLOTS OF $-1/\log y$ VS. $1/\sqrt{m}$



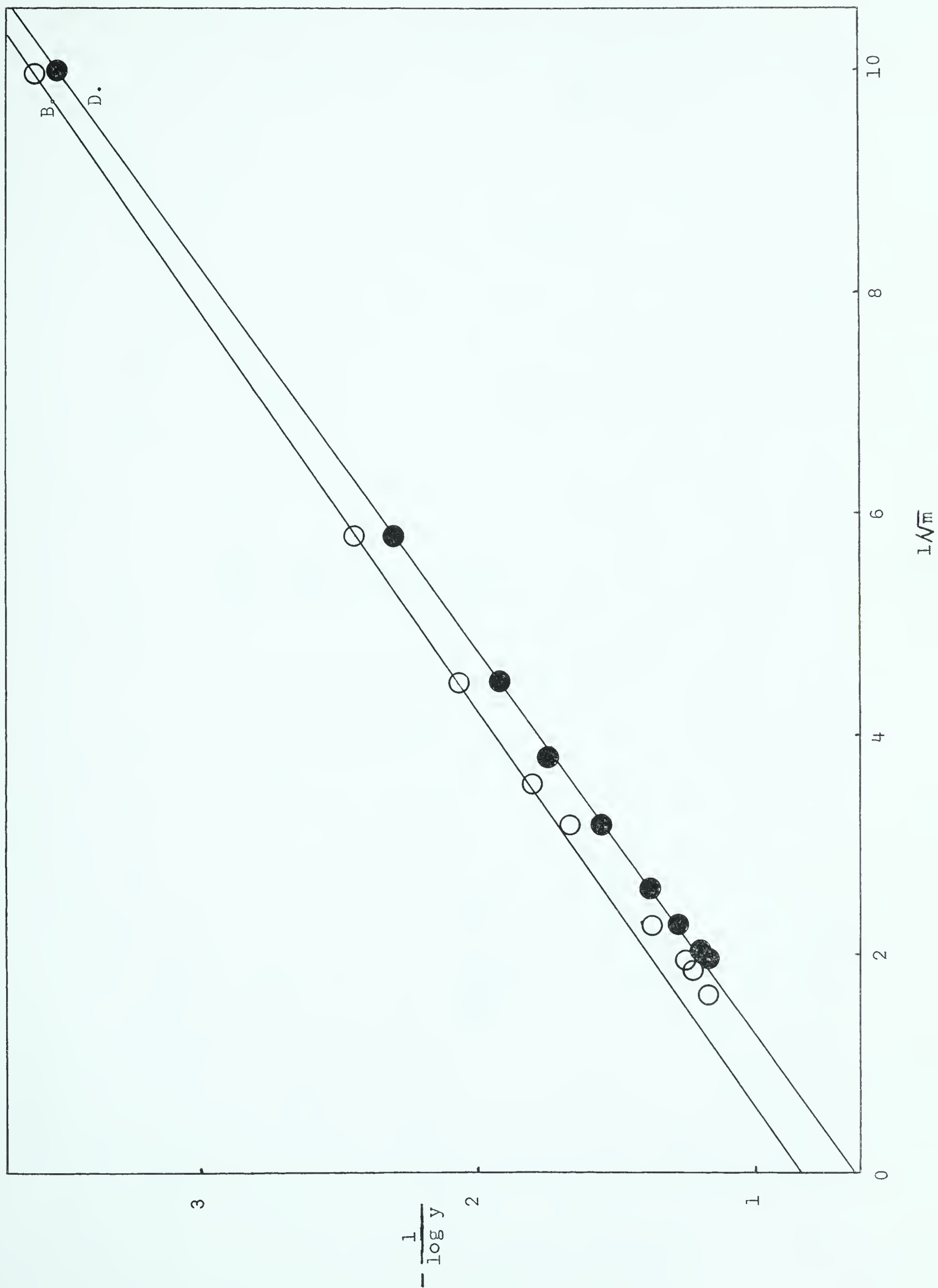
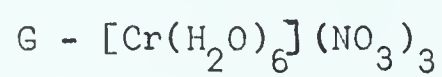


Figure 25

PLOTS OF $-1/\log y$ VS. $1/\sqrt{m}$



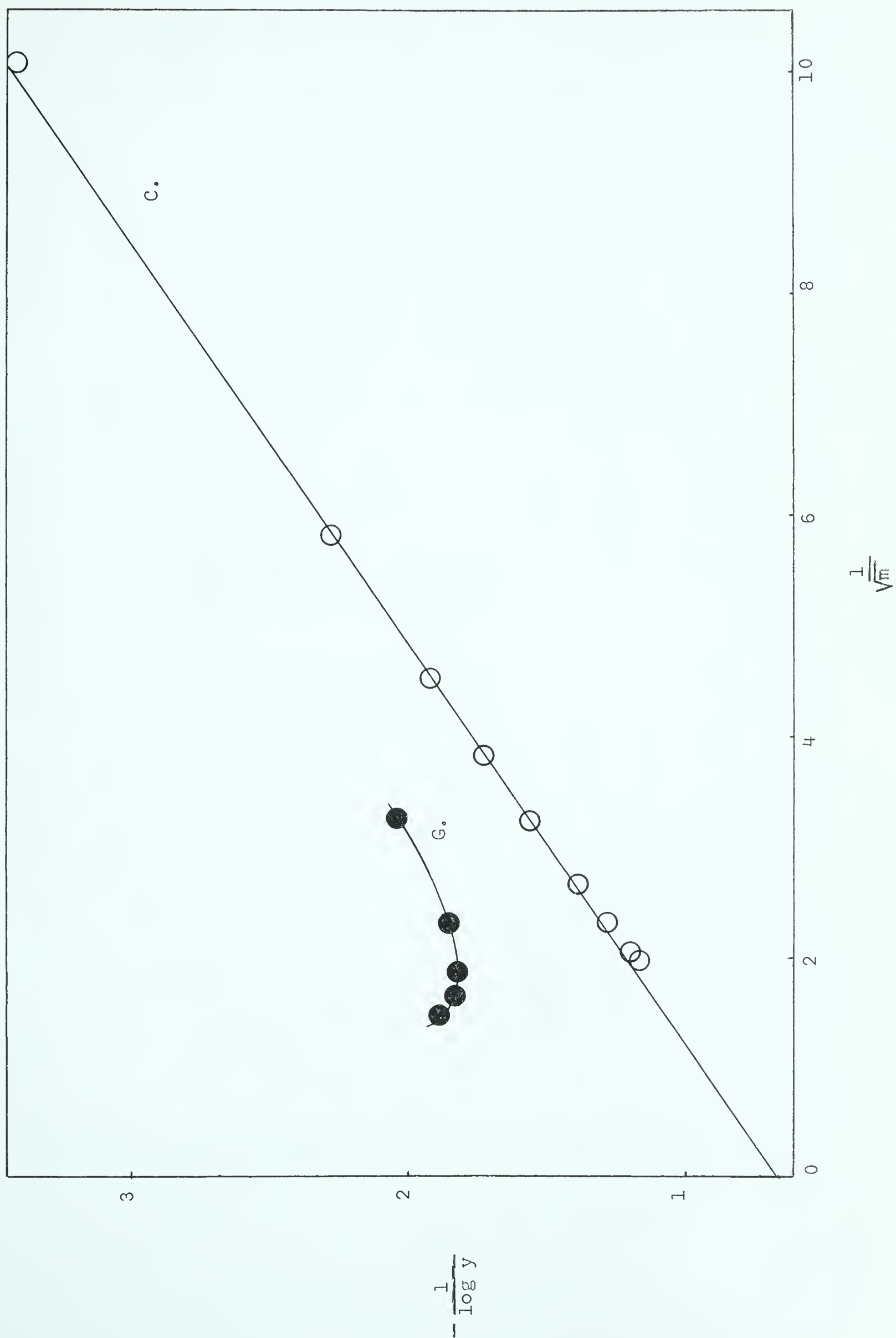
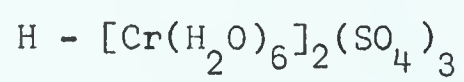
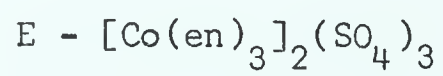
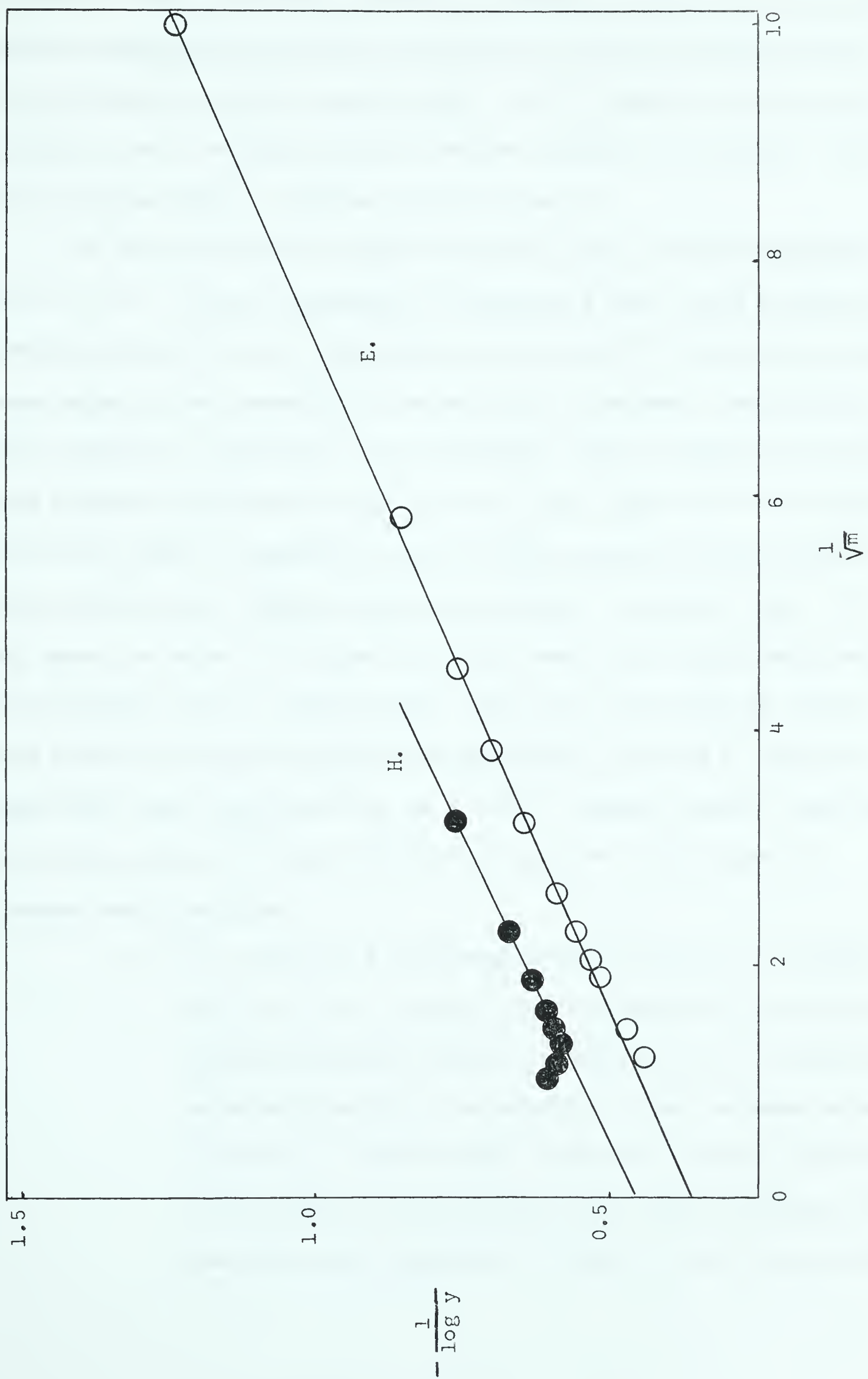


Figure 26

PLOTS OF $-1/\log y$ VS. $1/\sqrt{m}$





are included; these values were obtained by solution of the E.D.H.E. to which a quadratic concentration term had been added (56), and by solution of the Robinson and Stokes equation (equation XXVI) (55). Wherever available, the association or ion - pairing constants are also included in the table. The data of table XXI are also shown in figures 23, 24, 25 and 26.

Not all the results in tables XIX and XX show favourable agreement with the E.D.H.E. For many compounds no consistent \bar{a}^0 value could be obtained from solving the E.D.H.E. and consequently no calculated \bar{a}^0 values are reported. For some compounds the concentration range fitted is narrower than might be expected, notably for hydrochloric and hydrobromic acid and ammonium chloride. For some compounds the observed slope does not at all agree with the theoretical one, as in the cases of hydrofluoric acid, lithium chloride, sodium bromate, potassium chlorate, the cadmium halides, and sulfuric and selenic acid. In several cases the values of \bar{a}^0 appear to be low, such as for hydrofluoric acid, ammonium chloride, and the cadmium salts, while for a few compounds such as ammonium chloride and cupric sulphate the graphically obtained \bar{a}^0 values do not agree with those calculated from the E.D.H.E. However, several trends are evident in the results of tables XIX and XX as well as in the points of disagreement mentioned above:

- (a) The values of \bar{a}^0 calculated from the E.D.H.E. are without fail equal to or larger than those obtained from the more extended equations such as equation XXVI and the quadratic equation from (56). The solution of such extended equations consists of a set empirical constants, the exact values of which depend on the conditions under which correlation between theory and experiment is sought. The \bar{a}^0 values obtained

from the solution of such equations therefore can depend on such conditions as the definition of correlation in terms of precision and the concentration range over which this precision is found.

- (b) Compounds with a pronounced degree of association have slope values which are low compared to the theoretical slope values predicted, the most striking example being hydrofluoric acid. This is explained by the fact that the associated species contributes less to the ionic strength than do the separate component ions, and, as a consequence, the effective ionic strength is less than the apparent value.
- (c) There seems to be a tendency for less strongly hydrated electrolytes to have a slope which is slightly larger than the theoretically predicted one, notable examples being cesium chloride, sodium bromate, potassium chlorate, sodium and potassium nitrate. The significance of such a trend is not yet apparent.
- (d) In a few cases the E.D.H.E. appears to be valid at concentrations which are much greater than the generally accepted limit of validity, which is 0.1 M for 1 : 1 electrolytes and even less for other types of electrolytes (63). Compounds for which the slope agrees with the theoretical one and for which the concentration range fitted exceeds the generally accepted limit include sodium chloride, the potassium halides, rubidium chloride, lithium nitrate, calcium chloride, cupric chloride, barium hydroxide, sodium sulphate, cerium and lanthanum chloride, indium sulphate, and some of the coordination compounds of table XXI.

From the results it appears that, for the more ideal cases at least, the E.D.H.E. provides a means of estimating the mean molal activity coefficient, even at moderately high concentrations, for electrolytes which have a low tendency towards ion association.

The Activity Coefficient of Bromopentamminechromium(III) Bromide

The reliability of the estimation of the activity coefficient of bromopentamminechromium(III) bromide depends on the validity in moderately concentrated perchlorate solutions of the two principles involved, the E.D.H.E. and the Guggenheim treatment of mixed electrolyte solutions (64). The use of the E.D.H.E. to estimate the activity coefficient is encouraged by the results obtained for some of the compounds in tables XIX and XX and especially for the coordination compounds in table XXI. The correlation between the E.D.H.E. and the activity coefficient data for the coordination compounds listed in table XXI is shown in figures 23, 24, 25, and 26. The results seem to indicate that as a first approximation to the activity coefficient of bromopentamminechromium(III) bromide the E.D.H.E. might be used with an \bar{a} value of about 5 Å; values so calculated are shown in table XXII.

TABLE XXII

MEAN MOLAL ACTIVITY COEFFICIENTS OF BROMOPENTAMMINECHROMIUM(III) BROMIDE

CALCULATED FROM THE E.D.H.E. FOR $\bar{a}=5$

<u>c</u>	<u>\sqrt{c}</u>	<u>$-\log y$</u>	<u>y</u>
0.1	0.316	.293	.51
0.2	0.447	.347	.45
0.4	0.592	.389	.41
0.6	0.775	.426	.37 ₅
0.8	0.894	.445	.36
1.0	1.000	.458	.35
1.2	1.095	.469	.34
1.4	1.183	.478	.33
1.6	1.265	.485	.32 ₅
1.8	1.342	.491	.32
2.0	1.414	.496	.32

In the experimental procedure the total concentration of chromium(III) complex ion was about 10^{-3} M, while the perchlorate electrolyte concentration ranged from 0.1 - 5.0 M. Guggenheim (65) in his treatment of mixed electrolyte solutions has shown that the mean activity coefficient of one component of a solution containing two electrolytes should fall between the activity coefficients of the separate components at the same total concentrations. Furthermore, when one of the electrolytes is in large excess of the other, the activity coefficient of the more dilute electrolyte reaches a limiting value which lies crudely at the center of gravity of the activity coefficients of the separate components at the same total concentration. The existence of such a limiting value has been shown experimentally (66).

The activity coefficients of the perchlorate electrolytes used have been published (67) and are given in table XXIII. The activity coefficients of the perchlorate electrolytes as well as the values which were estimated for bromopentamminechromium(III) bromide in table XXII were plotted as a function of concentration in figure 27. Without quantitatively determining the "center of gravity" curves intermediate to the complex curve and each perchlorate electrolyte curve in figure 27 one might conclude that the appearance of such curves relative to each other will resemble the appearance of the perchlorate curves themselves relative to each other.

Qualitative comparison between the activity coefficients of the perchlorate electrolytes shown in figure 27 and the values of y_{MX} derived in section III and shown in figure 15 shows, if only crudely, a similarity between the relative positions of the perchlorate activity coefficient curves in figure 27 and y_{MX} curves for $n=15$ in figure 15.

The effect of the increase of electrolyte concentration on the

TABLE XXIII

THE MEAN MOLAL ACTIVITY COEFFICIENTS OF PERCHLORATE ELECTROLYTES*

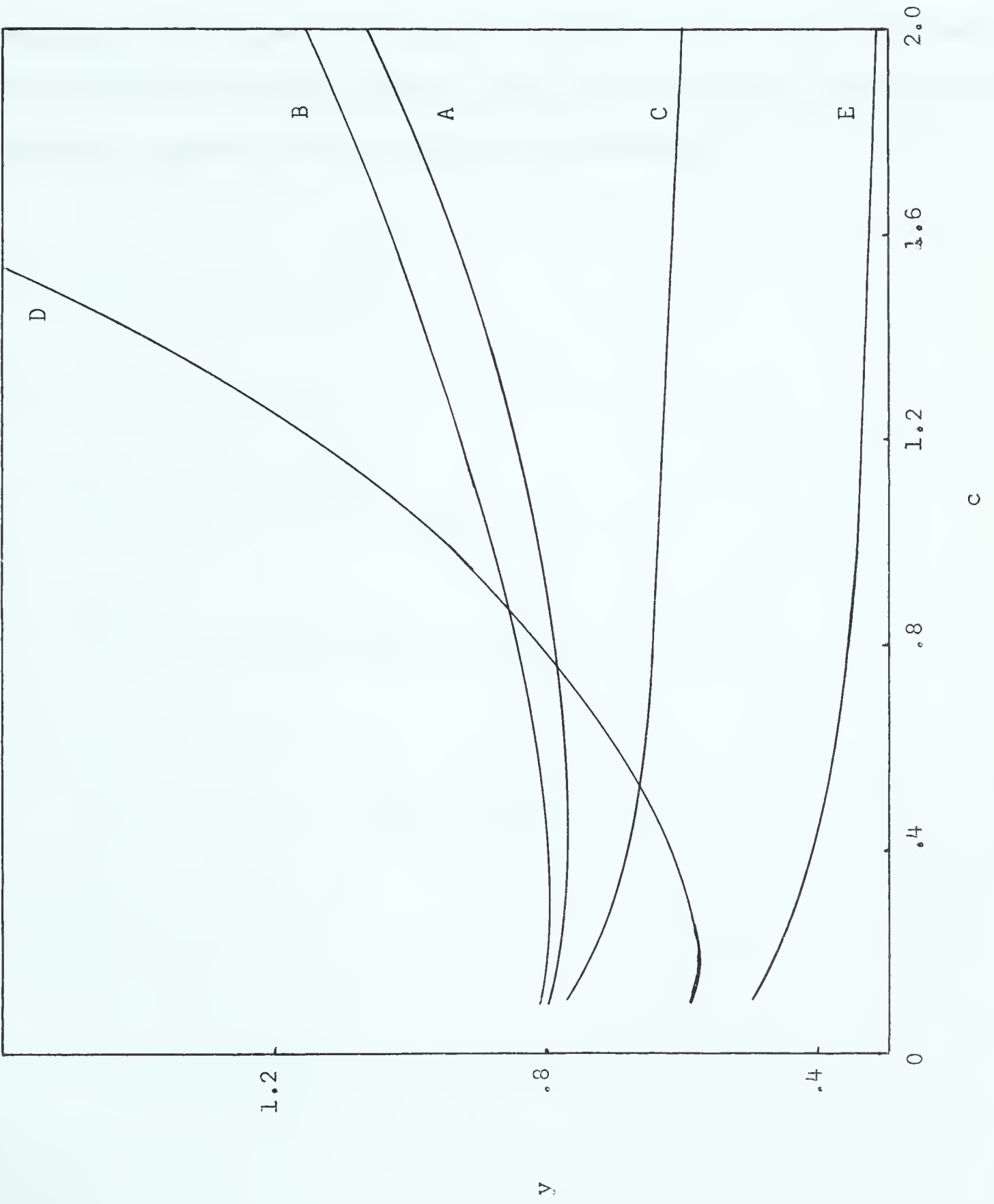
<u>c</u>	perchloric acid <u>y</u>	lithium perchlorate <u>y</u>	sodium perchlorate <u>y</u>	magnesium perchlorate <u>y</u>
0.1	.803	.812	.775	.590
0.2	.778	.794	.729	.578
0.3	.768	.792	.701	.589
0.4	.766	.798	.683	.613
0.5	.769	.808	.668	.647
0.6	.776	.820	.656	.688
0.7	.785	.834	.648	.739
0.8	.795	.852	.641	.798
0.9	.808	.869	.635	.868
1.0	.823	.887	.629	.946
1.2	.858	.931	.622	1.137
1.4	.900	.979	.616	1.385
1.6	.947	1.034	.613	1.705
1.8	.998	1.093	.611	2.13
2.0	1.055	1.158	.609	2.65

* Data from (67)

Figure 27

PLOTS OF MEAN ACTIVITY COEFFICIENT VS. CONCENTRATION

- A. Perchloric acid
- B. Lithium perchlorate
- C. Sodium perchlorate
- D. Magnesium perchlorate
- E. Bromopentamminechromium(III) bromide (estimated with E.D.H.E.)



rate of aquation of bromopentamminechromium(III) bromide so appears to be a pure electrolyte effect. An attempt to determine the nature of this electrolyte effect seemed to indicate a general participation of water in the reaction. This suggests that general solvation makes a more important contribution to the mechanism than any single water molecule, which agrees with the previously suggested solvent assisted S_N1 mechanism.

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